VOL. XXIV. [JUNE, 1902.] No. 6.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 61.]

THE ATOMIC WEIGHT OF ARSENIC.

BY W. CLARENCE EBAUGH.[1]

Received February 19, 1902.

INTRODUCTION.

IN the present state of our knowledge concerning the relative atomic weights of the elements, any additional evidence in regard to the generally accepted values will be welcomed. It is not enough to repeat old methods of determination and to follow out old lines of comparison. What is needed is the introduction of new analytical methods, new comparisons, and new ratios. In this way we can reenforce results obtained by earlier investigators or discover in them the existence of errors due to faulty methods of analysis or to impurities in the substances used in such investigations. It was with this guiding thought that the present redetermination of the atomic weight of arsenic was undertaken, and the result should be looked upon as a contribution to our knowledge of this constant. In no sense can it be regarded as conclusive, although in many respects it is certainly confirmatory.

[1] From author's thesis for Ph.D. degree, University of Pennsylvania, 1901.

In an earlier study of the atomic weight of arsenic, Hibbs[1] applied a method that has frequently been used with success in other determinations; *viz.*, the conversion of sodium pyroarsenate into sodium chloride in a current of hydrogen chloride gas. Thus a new ratio (NaCl : As) as well as a new factor (Na) was introduced into the calculations. It seemed desirable to extend this method to other arsenic-containing substances; therefore silver arsenate, lead arsenate, barium arsenate, magnesium pyroarsenate, sodium sulpharsenate and sodium cacodylate were prepared with the intention of converting them into the halogen salts of their respective metals. If practicable these halides were to be reduced to metal by heating them in a current of hydrogen. Thus we would have the ratios

$$Me_x Hal_y : As_z \text{ and } Me_x : As_z,$$

where Me represents silver, lead, barium, magnesium and sodium, and Hal represents chlorine, bromine and iodine. As additional factors there would be introduced oxygen, sulphur, carbon and hydrogen.

Much of the work was disappointing, but it is believed that the data gathered from the experiments, when the preconceived ideas were capable of execution, will be of value as a contribution to our knowledge concerning the atomic weight of arsenic.

HISTORICAL.

The atomic weight of arsenic has been studied by six investigators. Seven methods of attacking the problem were used.

It is astonishing how closely the result of Berzelius' single experiment (75.02) accords with the means of the series of experiments which followed. Dumas' first value (74.985) is also remarkable in view of the complicated method of investigation employed by him. Kessler, in a paper published in 1861, seems to throw doubt upon his own results (75.175), since he finds that they are influenced by (*a*) the time of contact of his solutions with the air, and (*b*) the dilution of the solutions used. Why Wallace should have obtained results more than 0.8 of a unit (74.229) lower than his predecessors, is inexplicable.

The generalizations of Van der Plaats, Ostwald, Seubert, Rich-

[1] Hibbs: Thesis, University of Pennsylvania, 1896.

ards, and Clarke, agree in assigning to arsenic the atomic weight 75, plus or minus a small probable error.

PREPARATION OF MATERIAL.

Silver Arsenate.—Silver nitrate was prepared from silver that had been subjected to the well-known purification method of Stas. Arsenious oxide was sublimed in an apparatus like that employed by Gattermann[1] in making aluminum chloride. The sublimed product was converted into arsenic acid by E. Kopp's method; *i. e.*, boiling 4 parts of arsenious oxide with 12 parts of nitric acid (sp. gr. 1.20) and 1 part of hydrochloric acid (sp. gr. 1.20). The arsenic acid was boiled down twice with an excess of nitric acid and then diluted to a definite volume. Ammonia water (sp. gr. 0.90) was boiled gently in a large flask, and the evolved ammonia led through an empty flask (which served as a condenser) into distilled water. The purified ammonium hydroxide and arsenic acid were then united in the proportions required to make triammonium arsenate. This solution was dropped gradually into a solution of silver nitrate; the precipitated silver arsenate was filtered out, washed thoroughly and dried at 150°-170° C.

Lead arsenate.—Disodium hydrogen arsenate (Merck) was recrystallized several times, dissolved in water and allowed to stand for some hours. Pure lead acetate of commerce was likewise subjected to three recrystallizations, dissolved in water and allowed to stand. The solution of lead acetate, filtered into a large beaker, was well diluted and treated with the filtered solution of disodium hydrogen arsenate. Constant agitation was maintained during the precipitation. The lead arsenate was allowed to subside and then washed by decantation until all soluble lead and alkali salts were removed. Drying at 150°-170° C. ensued.

Hydrogen Chloride Gas.—Concentrated sulphuric acid was dropped from a separatory funnel into hydrochloric acid (concentrated) contained in a 3-liter flask. The evolved hydrogen chloride gas was dried and purified by passing it through two sulphuric acid drying bottles and a calcium chloride tower.

Hydrogen Bromide Gas.—Two methods of preparation were tried. (*a*) Bromine was dropped slowly upon red phosphorus

[1] Gattermann: "Practical Methods of Organic Chemistry," Trans. 1898, p. 324.

covered with water. To remove the excess of bromine the gas was passed through two U-tubes containing glass beads and red phosphorus. (*b*) Pure resublimed anthracene was substituted for the red phosphorus and water used in method *a*. Anthracene placed in U-tubes removed free bromine. All bromine used during this investigation was rectified by two distillations over manganese dioxide and sulphuric acid.

Hydrogen Gas.—Concentrated sulphuric acid (1 part) and water (3 parts) slightly colored by platinic chloride were allowed to act upon granulated zinc. The hydrogen was purified by its passage through a series of wash bottles containing (*a*) water or ammoniacal silver nitrate; (*b*) potassium permanganate; (*c*) alkaline lead nitrate; (*d*) and (*e*) sulphuric acid.

DESCRIPTION OF APPARATUS.

The gases prepared as described above were led through combustion tubes of hard glass in which were placed porcelain boats containing the material to be experimented upon. The exit end of the tube dipped either into a receiver containing water or into a U-tube containing sulphuric acid. The latter opened directly into a draft chamber. The combustion tube was heated over Bunsen burners provided with fish-tail attachments; an additional burner held in the hand served to supply extra heat when necessary.

A short arm Troemner balance, sensitive to the thirty-fifth of a milligram and a set of weights, carefully standardized were used for all weighings. In every instance the observed weight was reduced to the vacuum standard and the means of the series of determinations, the probable errors, etc., were calculated according to the formulas given by Clarke.[1]

All atomic weights used were taken from F. W. Clarke's annual report to the American Chemical Society for the current year.[2]

EXPERIMENTAL PART.

I. Conversion of Silver Arsenate into Silver Chloride.—It was shown by Moyer[3] that arsenic could be completely separated from

[1] F. W. Clarke: "Recalculation of the Atomic Weights," p. 7.
[2] F. W. Clarke: This Journal, **23**, 94 (1901).
[3] Moyer: Thesis, University of Pennsylvania, 1896.

silver by heating silver arsenate in a current of hydrogen chloride gas. This fact was verified by the present author.

The method of procedure adopted was as follows: Dry silver arsenate was weighed out in a porcelain boat which was then placed in the combustion tube. A slow current of hydrogen chloride gas conducted through the tube gave rise to a vigorous reaction. Heat was evolved, the red-brown arsenate became yellowish white chloride and a deposit of water and arsenic trichloride appeared upon the inner walls of the tube. After half an hour a gentle heat was applied; when no further action could be observed the temperature was raised again, but not to such a degree as to cause the silver chloride to melt. At the close of the operation the silver chloride was barely fused, allowed to cool partially in the tube and then removed to a desiccator provided with anhydrous calcium chloride and soda lime. The desiccator and its contents were allowed to remain in the balance room for at least an hour before the boat was weighed. After weighing, the boat was reheated in a current of hydrogen chloride gas until the silver chloride was again fused. Cooling and weighing were carried out just as in the first instance. The analytical results follow:

Atomic weight of chlorine	35.45
Atomic weight of oxygen	16.00
Atomic weight of silver	107.92
Density of silver arsenate	5.77
Density of silver chloride	5.50

Silver arsenate. Grams.	Silver chloride. Grams.	Arsenic. Atomic weight.
0.23182	0.21547	74.987
0.47996	0.44615	74.944
0.52521	0.48820	74.956
0.80173	0.74517	74.996
0.94782	0.88083	75.061
1.02047	0.94830	75.083
1.03558	0.96258	74.974
1.05462	0.98014	75.033
Mean		75.004
Probable error		±0.012

II. Reduction of Silver Chloride to Metallic Silver.—The boat containing silver chloride, derived from silver arsenate as de-

scribed in the previous section, was covered with a strip ot platinum foil (to prevent possible loss by spirting) and placed in a combustion tube connected with the hydrogen supply. After the air contained in the apparatus was expelled by hydrogen a very gentle heat was applied. Gradually the temperature was raised until the tube was at a red heat. In this condition it was maintained for at least half an hour. If great care was not exercised during the first part of the operation, loss by spattering was sure to occur. Five to seven hours were required for a reduction. The boat, its contents and its cover were allowed to remain in the desiccator at the temperature of the balance room at least an hour before weighing. Reheating to redness, cooling and weighing ensured complete reduction. The silver obtained was arsenic-free and completely soluble in nitric acid. Results are given herewith:

Atomic weight of oxygen	16.00
Atomic weight of silver	107.92
Density of silver arsenate	5.77
Density of silver	10.57

Silver arsenate. Grams.	Silver. Grams.	Arsenic. Atomic weight.
0.23182	0.162175	75.027
0.47996	0.33583	74.950
0.52521	0.367525	74.907
0.80173	0.56099	74.936
0.94782	0.66318	74.959
1.02047	0.71400	74.964
1.05462	0.73771	75.082
Mean		74.975
Probable error		±0.015

III. Conversion of Silver Arsenate into Silver Bromide.—Silver arsenate was treated just as described under the first heading of the "Experimental Part" of this thesis, except that hydrogen bromide gas obtained from bromine and anthracene was substituted for hydrogen chloride gas. All due precautions against fusing were used, but it seemed that a little silver bromide always escaped when the last traces of arsenic were expelled. The weighing and other operations were conducted as outlined in previous sections. Variable results were obtained, most of them coming between 75.25 and 75.75. Two analyses yielded 74.984

and 74.967. The above determinations would serve well for ordinary quantitative analyses, but their lack of concordance bars them from use for atomic weight considerations. The silver bromide formed was arsenic-free.[1]

IV. Conversion of Lead Arsenate into Lead Chloride.—That arsenic could be completely eliminated from lead arsenate by the use of hydrogen chloride gas was proved by Hibbs[2]. In all of the following determinations, the lead chloride produced was examined for arsenic, but none was found.

Lead arsenate was weighed into porcelain boats. The boats and contents were heated to 150°-170° C. and again weighed. Hydrogen chloride gas was passed over the arsenate, at first in the cold, but afterwards at a gentle heat. A gradual increase in temperature was brought about and the current of gas was discontinued only after all action seemed to have ceased. In no case was the lead chloride fused. The usual precautions concerning cooling, weighing, reheating, etc., were followed out. The results obtained are:

Atomic weight of chlorine	35.45
Atomic weight of oxygen	16.00
Atomic weight of lead	206.92
Density of lead arsenate	6.29
Density of lead chloride	5.80

Lead arsenate. Grams.	Lead chloride. Grams.	Arsenic. Atomic weight.
0.38152	0.35381	74.988
0.436197	0.40449	75.016
0.57218	0.53065	74.964
0.60085	0.55717	75.020
0.74123	0.68736	75.010
0.77107	0.71494	75.067
0.88282	0.81858	75.054
0.97779	0.90674	75.054
Mean		75.022
Probable error		±0.009

Attempts were made to reduce lead chloride to metallic lead, by heating it in a current of hydrogen, but failed to give the desired

[1] Throughout the course of experiments it was found that the reactions in which hydrogen bromide was used gave more trouble than did those where hydrogen chloride was employed. Hydrogen iodide was more unsatisfactory than either of the preceding acids.

[2] Hibbs: *loc. cit.*

result. The temperature at which the chloride is reduced is so near that at which it is volatilized that the method is valueless. Careful heating for eight hours did not reduce all the lead chloride; some of it was found sublimed into the upper part of the boat. More lead chloride, mixed with black crystals of lead, was found adhering to the platinum cover placed over the boat.

V. Conversion of Lead Arsenate into Lead Bromide.—Preliminary experiments showed that the usual apparatus could be modified to advantage by inserting a stop-cock, through which air could be admitted to the combustion tube, in the neck of the U-tube preceding the combustion tube. By opening this cock the acid vapor could be diluted with air and thus the violence of the reaction was diminished. A filtering flask and suction pump attached to the exit receiver were also used.

The method employed in previous determinations was inapplicable here because the arsenic tribromide collecting in the boat was not readily expelled without loss due to spattering. The reaction took place violently in the cold, and bromine, water, and arsenic tribromide separated in large amounts.

As there were occasionally violent explosions when hydrogen bromide prepared from phosphorus, water and bromine was used,[1] and as phosphorus was found in the receiver, the method was abandoned for that employing anthracene and bromine. From this time no explosions occurred. Evidently the cause of the disturbance is to be looked for in the phosphorus used in the generator, hydrides of phosphorus being formed, rather than in the halide of arsenic, as was supposed by Meyer.[2]

The boat containing lead arsenate was placed in the combustion tube and heated to 200° C. Air mixed with hydrogen bromide was drawn through the apparatus and after all apparent action had ceased the heat was increased, but not to a point where fusion or volatilization of lead bromide could result. Cooling and weighing, reheating, cooling and weighing were carried out as usual. This manner of working prevented spattering, for the arsenic tribromide was removed as fast as it formed. The lead bromide was gray-white in color and contained no arsenic. Results follow:

[1] Chronologically this work preceded that described in Section III.

[2] Meyer: This Journal, 17, 735 (1895).

Atomic weight of bromine	79.95
Atomic weight of lead	206.92
Atomic weight of oxygen	16.00
Density of lead arsenate	6.29
Density of lead bromide	6.61

Lead arsenate. Grams.	Lead bromide. Grams.	Arsenic. Atomic weight.
0.59704	0.73092	75.066
0.61712	0.75567	74.967
0.65799	0.80569	74.980
Mean		75.004
Probable error		±0.021

The lead bromide could not be reduced quantitatively for reasons analogous to those given for the non-reduction of lead chloride (see Section IV).

Many attempts were made to convert barium arsenate into barium chloride, magnesium pyroarsenate into magnesium chloride and sodium sulpharsenate and sodium cacodylate into sodium chloride, but the results were of such a nature as to be useless in fixing the atomic value under discussion and may well be omitted here.

A summary of the results obtained during the course of this investigation follows:

	Arsenic. Atomic weight.	Probable error.
Ag_3AsO_4——-AgCl	75.004	±0.012
Ag_3AsO_4———-Ag	74.975	±0.015
$Pb_3(AsO_4)_2$——$PbCl_2$	75.022	±0.009
$Pb_3(AsO_4)_2$——$PbBr_2$	75.004	±0.021
Mean	75.008	
Probable error	±0.006	

This mean result, drawn from 26 determinations, affords another confirmation of the generally accepted atomic weight of arsenic. It may be interesting to note that 14 of the results lie below the general mean, while 12 of them lie above this value.

UNIVERSITY OF PENNSYLVANIA.

LECTURE EXPERIMENTS ILLUSTRATING VARIOUS TYPES OF CATALYTIC ACTION.

A. A. Noyes and G. V. Sammet.

Received March 11, 1909.

INTRODUCTION.

The experiments to be described in this article were devised as an accompaniment to two lectures upon the subject of catalysis.[1] It has been decided to publish them, as it is believed that the series as a whole may be of value in connection with lecture courses on theoretical chemistry, and that some of the separate experiments might be introduced into courses on inorganic and organic chemistry.

The experiments are presented in such a manner as to make their preparation and performance as easy as possible for the lecturer. As this involves the enumeration of many details, those who desire to obtain only a general view of the experiments here described are recommended to read, under each experiment, only the paragraphs entitled "Catalyzer", "Reaction Catalyzed" and "Observations", omitting those designated "Preparation" and "Experiment".

In accordance with the proposal of Ostwald, we understand the term *catalysis* to signify the *acceleration or retardation of a chemical reaction by substances which themselves undergo no permanent change as a result of their action.*

For convenience of consideration we distinguish the following important types or classes of catalytic agents:

1. Carriers; 2. Adsorbent contact agents; 3. Electrolytic contact agents; 4. Water; 5. Dissolved electrolytes; 6. Enzymes; 7. Inorganic colloids.

I. CATALYSIS BY CARRIERS.

By *carriers* are understood catalytic agents which are known to accelerate reactions through the formation of an intermediate compound with one of the reacting substances. Although it is

[1] Delivered before the North-eastern Section of the American Chemical Society and the Society of Arts of the Massachusetts Institute of Technology.

probable that some of the other types of catalytic agents (for example, enzymes) are in reality carriers, the term is here confined to those agents which are known to be such.

The experiments here described illustrate the action of carriers in the three states of aggregation, gaseous, liquid, and solid.

The suggestion of Wagner[1] that carrier-actions be designated pseudo-catalyses, thereby implying that they are not true cases of catalysis, seems to us an unfortunate one. There has always been a tendency to attach to the term catalysis a mysterious significance, which would be continued if the term is still to be confined to *unexplained* accelerating actions. The advantage of Ostwald's definition is that it is a concrete, experimental one, having no reference whatever to the way in which the acceleration is brought about.

Experiment 1.

Catalyzer.—Nitric oxide.

Reaction Catalyzed.—$2SO_2 + O_2 = 2SO_3$.

Preparation of the Experiment.—Graduate roughly, a long, narrow bell-jar of about 500 cc. capacity by marking lines upon it with a blue pencil at points corresponding to $^6/_{15}$ and $^{11}/_{15}$ of its total volume measured from the closed end of the jar. Rinse the jar with water so that the inner sides of it will be wet; fill it with mercury, and invert it over a long narrow trough, also filled with mercury, and having a deep longitudinal groove in the bottom. Introduce sulphur dioxide into the jar until the meniscus falls to the upper mark; then introduce, by means of a bent tube, enough water barely to cover the surface of the mercury. Connect the bent tube with a gasometer or cylinder of oxygen by means of a rubber tube. Fill two short, wide test-tubes with mercury, and invert them over the trough. Introduce into one of these tubes a volume of nitric oxide equal to 0.1 of the total volume of the bell-jar, and into the other tube one-half this amount of nitric oxide.

Experiment.—Introduce into the bell-jar oxygen from the gasometer or cylinder, until the mercury meniscus falls to the second mark. Place the mouth of the test-tube containing the larger amount of nitric oxide in the groove beneath that of the bell-jar,

[1] *Ztschr. phys. Chem.*, **28**, 78.

and tip the tube until the gas has passed into the jar. After the mercury has nearly stopped rising, introduce in the same way into the jar the nitric oxide gas in the second tube.

Observations.—No change occurs on adding the oxygen to the sulphur dioxide. When the nitric oxide is introduced, the gas reddens and begins to contract and become filled with white fumes. A white deposit (nitrosylsulphuric acid) soon forms on the sides of the jar. The contraction nearly ceases after 30 to 40 seconds, but becomes rapid again when the second portion of the nitric oxide is introduced. The volume finally becomes constant at about 0.2 of the total volume of the jar.

Experiment 2.

Catalyzer.—Sulphuric acid.

Reaction Catalyzed.—$2C_2H_5OH = (C_2H_5)_2O + H_2O$.

Preparation of the Experiment.—Connect a 500 cc. distilling flask with a Liebig condenser which is fitted with an adapter delivering into a 200 cc. graduate. Place in the flask 135 cc. of concentrated sulphuric acid, and add slowly 75 cc. of alcohol. Insert a 2-hole rubber stopper holding a thermometer and a 150 cc. drop-funnel, both of which reach nearly to the bottom of the flask. Fill the drop-funnel with alcohol, and, just before the lecture, heat the liquid in the flask to 140°-150°; then allow the alcohol to flow slowly into the flask at such a rate that the distillate drops rapidly into the graduate.

Experiment.—Add to the ether which has collected in the graduate 2 cc. of powdered potassium carbonate, and shake. After the layers have formed pour the top layer into a 200 cc. graduate which contains 75 cc. of water, and shake.

Observations.—The alcohol is continuously converted to ether, which comes over in the distillate and holds the water which is also produced by the reaction in solution; but on adding the potassium carbonate the distillate separates into two layers consisting of about 5 cc. of water to 100 cc. of ether. On pouring the upper layer into water, it does not mix with it, showing that the distillate is mainly ether, and not alcohol.

Experiment 3.

Catalyzer.—Ferric bromide.

Reaction Catalyzed.—$C_6H_6 + Br_2 = C_6H_5Br + HBr$.

Preparation of the Experiment.—Support a 250 cc. distilling flask upon a lamp-stand and connect its side-arm with a funnel whose mouth dips just below the surface of a caustic potash solution. Place in the flask 4 cc. of bromine. Provide a cork stopper for the flask, a long-necked funnel, a small wash-bottle, like that used in Experiment 2, containing strong ammonia, 30 cc. of benzene in a small bottle, and 0.5 cc. of powdered iron.

Experiment.—Pour into the distilling flask the 30 cc. of benzene; then add the 0.5 cc. of powdered iron. Blow ammonia gas from the wash-bottle over the neck of the distilling flask. Finally insert the cork.

Observations.—No action occurs between the benzene and bromine alone, but a vigorous boiling up and great clouds of white fumes are observed as soon as the iron is added.

Experiment 4.

Catalyzer.—Aluminum chloride.

Reaction Catalyzed.—$C_6H_6 + CH_3COCl = C_6H_5COCH_3 + HCl$.

Preparation of the Experiment.—Place a 250 cc. distilling flask in a clamp on a lamp-stand. Connect the side-arm with a funnel that dips just beneath the surface of a potash solution. Pour into the flask 10 cc. of acetyl chloride. Provide a cork stopper for the flask, a long-necked funnel, 50 cc. of benzene in a small bottle, 10 cc. of powdered sublimed aluminum chloride in a corked test-tube, and a small wash-bottle of strong ammonia with a rubber syringe bulb attached to the longer tube.

Experiment.—Pour into the flask through the funnel the 50 cc. of benzene, then add the 10 cc. of aluminum chloride. Blow from the wash-bottle ammonia gas over the mouth of the flask, and finally insert the cork.

Observations.—No action occurs between the benzene and acetyl chloride alone, but a vigorous effervescence and copious evolution of white fumes occur soon after the aluminum chloride is added.

Experiment 5.

Catalyzer.—Platinum foil.

Reaction Catalyzed.—$2CH_3OH + O_2 = 2CH_2O + H_2O$.

Preparation of the Experiment.—Pour into a 300 cc. beaker a layer of methyl alcohol 1 cm. deep. Cover the beaker with a perforated watch-glass in whose perforation is a cork stopper from which a star made of platinum foil hangs down by a platinum wire 2 to 3 cm. above the surface of the alcohol.

Experiment.—Ignite the methyl alcohol vapor in the beaker by applying the flame of a burner to it, and raise one side of the watch-glass a few millimeters by inserting a bit of wood or rubber tube.

Observations.—The platinum star glows brightly when the amount of air admitted to the beaker is properly adjusted.

2. CATALYSIS BY ADSORBENT CONTACT AGENTS.

By adsorbent contact agents we understand solid substances that accelerate reactions by the adsorption on their surfaces of one or more of the reacting substances. Whether the acceleration is due to an increase in the concentration of the reacting substances, or to an activation of them, or to a chemical combination constituting a carrier action, is not thereby taken into consideration.

The experiments to be here presented refer mostly to gaseous mixtures, but include one dissolved substance (hydrogen peroxide).

Experiment 6.

Catalyzer.—Platinum.

Reaction Catalyzed.—$2xNH_3 + yO_2 = 3xH_2O + zN_2 + wNO$.

Preparation of the Experiment.—Place in a wide-necked bottle of about 250 cc. capacity, 75 cc. of concentrated ammonia-water (sp. gr., 0.90). Insert a delivery tube, which is connected to a tank of oxygen, so that it dips below the surface of the ammonia-water. Wind one end of a platinum wire (about 0.5 mm. diameter) around a match, leaving the other end so long that, when the match is supported across the mouth of the bottle, the end will be about 1 cm. above the surface of the liquid.

Experiment.—Heat the platinum wire in a flame, and insert it while hot into the flask. After a few seconds turn on a moderately rapid current of oxygen.

Observations.—Almost immediately after introducing the platinum wire into the flask, it begins to glow. When the oxygen is bubbled through the ammonia, the platinum glows more brightly, and the flask becomes filled with white fumes; and after a few seconds an explosion is produced.

Experiment 7.

Catalyzer.—Platinum.

Reaction Catalyzed.—$2SO_2 + O_2 = 2SO_3$.

Preparation of the Experiment.—Place about 5 grams of loose asbestos on a filter plate and pour through it a 10 per cent. hydrochlorplatinic acid solution until the asbestos is saturated with it. Transfer it to a large porcelain crucible, and ignite strongly for thirty minutes, disintegrating the mass from time to time. Pack loosely with the platinized asbestos a piece of combustion tubing about 45 cm. long, to within 4 or 5 cm. of one end and 20 cm. of the other. Place the tube in a short furnace with 2 or 3 burners, and connect one end by means of rubber stoppers and a delivery tube to one of the necks of a three-necked Woulff bottle which is charged to a depth of 2 or 3 cm. with concentrated sulphuric acid. The other two necks of the Woulff bottle are connected by means of rubber stoppers and delivery tubes which dip below the surface of the sulphuric acid in the Woulff bottle, to an oxygen cylinder and a sulphur dioxide generator, respectively. The sulphur dioxide is produced by dropping strong sulphuric acid from a drop funnel into a flask containing strong commercial sodium bisulphite solution. The other end of the combustion tube is fitted with a rubber stopper carrying a T-tube, of which the perpendicular arm is closed by a piece of rubber tubing and a pinch-cock. The straight end of the T-tube is joined to a condensation-tube (such as is used for sulphur dioxide), the bulb of which is placed in a dish of ice. The outlet of the condensation-tube is connected to a funnel, the mouth of which dips only a little below the surface of a potash solution.

Experiment.—Pass the oxygen and sulphur dioxide at a moderate rate through the tube so that the sulphur dioxide bubbles through the sulphuric acid about twice as fast as the oxygen. Light the burners beneath the empty part of the tube, and heat it to just below redness; after a minute or two, open the pinch-cock momentarily to show that no combination is taking place. Then push the tube along so that the platinized asbestos is brought over the flame, and, after the tube has become hot, open the pinch-cock on the T-tube for a moment. Continue the experiment for fifteen minutes or more, and then remove the condensation-tube from the ice-bath.

Observations.—No white fumes are seen on opening the pinch-cock until the platinized asbestos is heated. After about fifteen minutes the condensation-tube will be coated with white crystals.

Experiment 8.

Catalyzers.—Platinum black and bone-black.

Reaction Catalyzed.—$2H_2O_2 = 2H_2O + O_2$.

Preparation of the Experiment.—Place in each of two lecture test-tubes 25 cc. of commercial, concentrated hydrogen peroxide solution which has been made very slightly alkaline by the addition of ammonia. Soak two 9-cm. filter-papers in a 10 per cent. hydrochlorplatinic acid solution; dry the filter papers and ignite them in a large porcelain crucible until the carbon is all burned off. Place the reduced platinum in a small test-tube. Provide also 1 cc. of bone-black and a splinter of wood.

Experiment.—Add the reduced platinum to one portion of hydrogen peroxide solution and the bone-black to the other portion. Ignite the wood-splinter in a flame until one end of it glows when removed from the flame, and insert it in turn into each of the test-tubes.

Observations.—When the platinum black and the bone-black are added to the hydrogen peroxide a violent effervescence ensues and the glowing splinter becomes ignited.

3. CATALYSIS BY ELECTROLYTIC CONTACT AGENTS.

Electrolytic contact agents are those catalytic agents which

accelerate reactions in which metals are involved through the formation of a voltaic couple. They are themselves in all cases metallic substances. Two experiments are given below, illustrating their action in case of an inorganic and of an organic reaction, respectively.

Experiment 9.

Catalyzer.—Platinum.

Reaction Catalyzed.—$Sn + 2HCl = SnCl_2 + H_2$.

Preparation of the Experiment.—Fit a 300 cc. Erlenmeyer flask with a rubber stopper provided with a thistle-tube and a delivery-tube, the end of which dips into a beaker of water. Cover the bottom of the flask to a depth of 2 cm. with a layer of pure feathered tin. Provide a medicine dropper, some hydrochloric acid of 1.12 sp. gr., and a little 10 per cent. hydrochlorplatinic acid solution.

Experiment.—Pour into the flask through the thistle-tube enough hydrochloric acid to entirely cover the tin; then add 5 or 6 drops of the platinum solution and shake.

Observations.—Only a very slight action occurs between the tin and acid alone; but a vigorous effervescence and rapid evolution of gas occur soon after the platinum solution is added.

Experiment 10.

Catalyzer.—Copper.

Reaction Catalyzed.—$C_2H_4Br_2 + Zn = C_2H_4 + ZnBr_2$.

Preparation of the Experiment.—Place 20 cc. of absolute alcohol and 20 cc. of ethylene bromide in a lecture test-tube whose mouth is fitted with a cork carrying a straight piece of (5 mm. wide) delivery tubing. Provide 2 cc. of granulated zinc in a test-tube, a little saturated solution of crystallized copper chloride in alcohol, and a beaker of ice water.

Experiment.—Pour the zinc into the test-tube, then add 3 cc. of the copper chloride solution, insert the cork, and shake. As soon as the effervescence becomes very vigorous, so that the air has been completely expelled, light the gas issuing from the tip of the

delivery tube. When the action becomes too violent, place the test-tube in the beaker of ice water.

Observations.—No action occurs between the ethylene bromide and zinc alone, but a vigorous effervescence begins in about ten or fifteen seconds after the addition of the copper chloride, and a large jet of flame is produced when the gas is ignited.

4. CATALYSIS BY WATER.

Water is a substance whose presence in at least minute amounts seems to be essential to the occurrence of most chemical reactions. Moreover, its method of action is probably unique, consisting either in a hydration or electrolytic dissociation of the reacting substance. It is therefore not inappropriate that it alone constitutes a type of catalytic agent.

Four experiments illustrating its action on gaseous, liquid, and solid reacting mixtures, and on a solid-gaseous mixture, are here described.

Experiment 11.

Catalyzer.—Water.

Reaction Catalyzed.—$2H_2S + SO_2 = 2H_2O + 3S$.

Preparation of the Experiment.—Fit a thoroughly dry glass balloon with a cork stopper with four holes carrying two dry delivery tubes leading to the bottom of the balloon and a third one terminating just below the stopper. All of these tubes should be bent at right angles above the stopper. Connect one of the long tubes with a tower filled with calcium chloride, which in turn is connected with a gas wash-bottle containing dilute sulphuric acid (1:3), which last is connected with a Kipp hydrogen sulphide generator. Connect the other long tube through two gas wash-bottles containing concentrated sulphuric acid, with a sulphur dioxide gasometer, or a generator in which sulphur dioxide is made by dropping concentrated sulphuric acid into a strong solution of commercial acid sodium sulphite. Connect the third delivery tube with a funnel whose mouth dips a little below the surface of a strong caustic potash solution. Close the fourth hole of the stopper with a piece of glass rod. Pass the two gases into the

balloon for ten to fifteen minutes, running the hydrogen sulphide about twice as fast as the sulphur dioxide. (The experiment may fail if the sulphur dioxide is in considerable excess.) Place a 250 cc. flat-bottom flask upon a tripod with a burner beneath. Fill it one-third full of water and fit it with a rubber stopper provided with a delivery tube, so bent that its outer end can be easily inserted in the fourth hole of the stopper of the balloon. Regulate the flame of the burner so that the water is kept barely boiling.

Experiment.—Cause the two gases to flow into the balloon for half a minute. Then remove the piece of glass-rod, insert the delivery tube leading from the flask of boiling water, and allow the steam to flow into the balloon for a few seconds.

Observations.—Nothing occurs on mixing the two gases in the dry state. After introducing the steam, sulphur at once begins to deposit on the walls of the balloon, and, in the course of half a minute, completely covers them.

Experiment 12.

Catalyzer.—Water.

Reaction Catalyzed.—$I_2 + H_2S = 2HI + S$.

Preparation of the Experiment.—Place 250 cc. of commercial sodium-distilled ether in a 500 cc. glass-stoppered bottle. Dissolve in this 0.35 gram of iodine and saturate the solution with hydrogen sulphide by passing through it for ten minutes a slow current of gas, generated in a Kipp generator and dried by being passed first through a gas wash-bottle containing dilute sulphuric acid (1:3) and then through a drying tower filled with calcium chloride. Place the hydrogen sulphide apparatus upon the lecture table. Measure out 3 cc. of water in a small graduate.

Experiment.—Pass a slow current of hydrogen sulphide into the ethereal solution of iodine for half a minute. Add 3 cc. of water to the ether solution and shake thoroughly.

Observations.—Decolorization of the dry ethereal solution of iodine is caused only very slowly by the hydrogen sulphide, but takes place very rapidly when the water is added.

Experiment 13.

Catalyzer.—Water.

Reaction Catalyzed.—$Zn + I_2 = ZnI_2$.

Preparation of the Experiment.—Place 4 cc. of powdered iodine in a test-tube and 2 cc. of zinc dust in a 25 cc. glass-stoppered wide-mouthed bottle. Place a carbon-funnel in the mouth of a 4-liter glass balloon supported on a suitable ring. Provide a wash-bottle delivering a fine stream.

Experiment.—Pour the iodine into the bottle containing the zinc dust and shake. Then pour the mixture onto the bottom of the balloon and direct a stream from the wash-bottle upon it.

Observations.—On the addition of water to the dry mixture of the zinc dust and powdered iodine, a violent action takes place attended by a sizzling and evolution of violet vapors of iodine, which entirely fill the balloon.

Experiment 14.

Catalyzer.—Water.

Reaction Catalyzed.—$2Na + Cl_2 = 2NaCl$.

Preparation of the Experiment.—Fill a piece of combustion tube 100 cm. long, which has been dried by flashing with a flame, quickly with phosphorus pentoxide for $^2/_3$ of the distance from one end of the tube, using ignited asbestos plugs to hold it in place. The delivery tube from a gasometer of chlorine is joined to a T-tube, one branch of which is connected with a rubber tube (provided with a pinch-cock) long enough to reach to the empty end of the combustion tube; the other branch of the T-tube leads through two gas-wash-bottles containing sulphuric acid to the filled end of the combustion tube, which is fitted with a rubber stopper carrying a Y-tube, of which the third branch leads through a rubber tube provided with a pinch-cock to a funnel dipping under strong caustic potash solution. Fit the empty end of the combustion tube with a perforated stopper carrying a small delivery tube. Pass chlorine at a slow rate for half an hour through the sulphuric acid bottles and the combustion tube, which is inclined somewhat so that the gas enters at the lower end.

While the chlorine is passing, flash the empty part of the combustion tube for some minutes with a flame in order to dry it completely. Provide a Bunsen burner, a small porcelain boat, a pair of pincers, several pieces of sodium of the size of a pea, and a stout wire with a hook at one end for removing the boat from the combustion tube.

Experiment.—Start a slow current of chlorine through the combustion tube. Place in the porcelain boat three or four pieces of sodium. Ignite the sodium by heating the boat in the flame of the burner and push it into the empty part of the combustion tube. Draw the boat back into the air for a moment, and again push it into the tube; then insert the stopper, connect the delivery tube in it with the rubber tube leading directly to the chlorine generator, and open the pinch-cock upon it. Open the pinch-cock on the tube leading into the potash solution, and pass a rapid current of the undried chlorine over the sodium through the tube in the reverse direction to that of the previous current.

Observations.—When the burning sodium is inserted in the dry chlorine, it is extinguished. When drawn back into the air, it becomes again ignited, and is again extinguished on pushing it back into the dry chlorine. When the moist chlorine is passed over it, it burns with great brilliancy.

5. CATALYSIS BY DISSOLVED ELECTROLYTES.

Dissociated substances in aqueous solution exert a variety of catalytic actions. The most important of these is that exerted upon reactions of hydrolysis by acids in virtue of their hydrogen ions.[1] This is illustrated by an experiment on the saccharification of starch by sulphuric acid.

Another variety of catalytic action by electrolytes is the great retardation of reactions involving weak acids, by their neutral salts,—a phenomenon explained by the Ionic Theory and the Law

[1] We desire to take this opportunity to suggest what seems to us a plausible hypothesis in regard to the action of hydrogen ions: that is, that these ions are hydrated and that the water in combination with them is more reactive than ordinary water; in other words, that the hydrogen ions act as water-carriers. While there is at present no experimental evidence in favor of this hypothesis (or of any other), the fact that it is an entirely reasonable one shows that one of the purest types of catalytic action may be in reality only a carrier action.

of Mass-Action. A lecture experiment illustrating this has been already described in detail in this Journal.[1]

Still another variety of such catalytic actions is the highly specific influence on reactions of oxidation and reduction of certain dissociated substances, especially of those which are themselves capable of undergoing oxidation or reduction. An experiment on a reaction of this kind has been earlier presented.[2]

Finally is to be mentioned a type of action which electrolytes exert apparently as a direct consequence of the electric charges upon the ions, namely, the coagulation of colloidal solutions and fine suspensions. Although this is not in a strict sense a catalytic action, since according to recent experiments[3] a minute quantity of the electrolyte is decomposed and precipitated with the colloid, yet the coagulative effect produced is so great in comparison with the quantity of electrolyte consumed that it has, from a practical standpoint, the characteristics of a catalysis. We have therefore included an experiment showing both the coagulation of colloidal arsenic sulphide by salts and the much greater coagulating effect upon it of bivalent than of univalent positive ions.

Experiment 15.

Catalyzer.—Sulphuric acid.

Reaction Catalyzed.—$(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6$.

Preparation of the Experiment.—Place 2 cc. of starch in each of two lecture test-tubes. Measure out in small graduates two 5 cc. portions of Fehling's solution, 25 cc. of a 5 per cent. sulphuric acid solution and enough strong caustic potash solution to neutralize this acid (9 cc. of 50 per cent. potash).

Experiment.—Add the 25 cc. of acid to the starch in one of the test-tubes and 25 cc. of water to that in the other, and boil both for about half a minute. Neutralize the acid solution with the potash. Bring the contents of both test-tubes to a boil, then add 5 cc. of Fehling's solution to each, and bring to a boil again.

Observations.—On addition of the Fehling's solution a heavy

[1] This Journal, **22**, 744.

[2] *Ibid.*, **22**, 742.

[3] Linder and Picton: *J. Chem. Soc.*, **67**, 63 (1895); Whitney and Ober: This Journal, **23**, 842 (1901).

red precipitate is thrown out in the tube in which the starch was boiled with the acid, but the blue color of the solution is not discharged in the other tube containing only starch and water.

Experiment 16.

Catalyzers.—Barium chloride and sodium chloride.

Reaction Catalyzed.—As_2S_3 (colloid) = As_2S_3 (precipitate).

Preparation of the Experiment.—Saturate 250 cc. of cold distilled water with hydrogen sulphide, and add to it gradually (that is, within two or three minutes) a solution of 5 grams of arsenious oxide in 250 cc. of water, keeping the hydrogen sulphide passing into the solution during the addition. Filter this solution. Place 200 cc. of it in each of two lecture jars provided with glass stirring rods. Prepare 100 cc. of a half-normal solution of barium chloride and also of one of sodium chloride.

Experiment.—Add to the colloid in one jar 3 cc. of the barium chloride solution, stirring constantly. To the other colloid, add 25 cc. of the sodium chloride solution, and after waiting about a minute, add 40 cc. more.

Observations.—On addition of the salt solutions to the colloid, immediate coagulation of arsenious sulphide takes place in the solution to which the barium chloride was added, and on waiting a minute or so, the precipitated sulphide settles in this solution, while no change takes place in the colloid to which the sodium chloride was added. On the addition of the second portion of sodium chloride, however, this solution also coagulates.

6. CATALYSIS BY ENZYMES.

Enzymes are complex organic substances of animal or vegetable origin which exert a variety of catalytic actions. Enzymes may be classified as hydrolyzing, oxidizing, molecule-splitting, synthesizing, and coagulating, according to the nature of the reaction which they catalyze. Experiments are described below illustrating the first, third, and fifth of these classes; namely, the hydrolysis of starch by ptyalin and of a glucoside by emulsin, the decomposition of hydrogen peroxide by blood, and the coagulation

of casein by rennet. The decomposition of hydrogen peroxide is produced by enzymes of all kinds, and is therefore not a good example of a specific molecule-splitting enzyme. A far better one would be the decomposition of sugar into alcohol and carbon dioxide by zymase, the recently discovered enzyme to which the action of yeast has been shown to be due; but its separation from the yeast-cells is a matter of some difficulty.[1] The hydrogen peroxide experiment is introduced here partly for the sake of illustrating the retarding effect which poisons exert on enzyme-action.

Experiment 17.

Catalyzer.—Ptyalin.

Reaction Catalyzed.—$(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6$.

Preparation of the Experiment.—Place in a lecture test-tube an amount of corn-starch of the volume of a split pea. Provide 25 cc. of fresh saliva and a little 1 per cent. iodine solution. (Secretion of saliva in the mouth may be greatly promoted by chewing a piece of paraffin.)

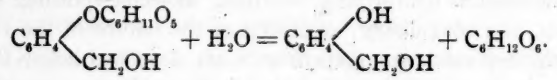
Experiment.—Add 10 cc. of water to the starch and heat it to boiling. Add 10 cc. more of cold water and 2 or 3 drops of the iodine solution; then add the 25 cc. of saliva. When decolorized, add a few more drops of iodine.

Observations.—The starch solution becomes of a deep blue color on the addition of the iodine, and this disappears almost immediately on addition of the saliva and is not restored when the second portion of iodine is added.

Experiment 18.

Catalyzer.—Emulsin.

Reaction Catalyzed.—



Preparation of the Experiment.—Dissolve 10 cc. of powdered salicine in 75 cc. of water. Place half of this solution in each of

[1] See Effront: "Enzymes and their Applications," Prescott's Translation, p. 277.

two lecture test-tubes. Rub 0.25 gram of emulsin to a fine powder in a mortar and treat it with 20 cc. of warm water; allow it to stand for some hours and then filter it. Pour one-half of the emulsin solution into each of two small test-tubes. Measure out two 5 cc. portions of Fehling's solution.

Experiment.—Add to one of the test-tubes containing the salicine one-half of the solution of emulsin, warm gently (not above 50°), and allow to stand for more than a minute. In the meantime, heat the rest of the emulsin to boiling for half a minute, add it to the other half of the salicine, and heat the mixture to boiling. Then heat the other tube of salicine and emulsin to boiling, add 5 cc. of Fehling's solution to each tube, and bring to a boil again.

Observations.—On boiling with Fehling's solution, scarcely any change takes place in the salicine solution to which the emulsin destroyed by boiling was added, but decolorization and formation of a red precipitate take place in the other salicine solution which was treated with the unboiled emulsin.

Experiment 19.

Catalyzers.—Blood and blood + potassium cyanide.

Reaction Catalyzed.—$2H_2O_2 = 2H_2O + O_2$.

Preparation of the Experiment.—Place in each of two lecture test-tubes 25 cc. of hydrogen peroxide. Provide 2 cc. of saturated potassium cyanide solution, some fresh blood, and a medicine dropper.

Experiment.—To one tube of hydrogen peroxide add 5 or 6 drops of the potassium cyanide solution, then add to each tube 4 or 5 drops of blood.

Observations.—A very vigorous effervescence and a voluminous frothing occur in the tube of hydrogen peroxide to which blood alone was added, while in the one to which the cyanide was added only a slight action takes place.

Experiment 20.

Catalyzer.—Rennet.

Reaction Catalyzed.—Casein (colloid) = Casein (precipitate).

Preparation of the Experiment.—Place 200 cc. of skimmed milk in a lecture jar. Provide some commercial liquid rennet.

Experiment.—Add 30 cc. of the rennet to the milk, and stir.

Observations.—Almost immediate coagulation of the milk occurs.

7. CATALYSIS BY INORGANIC COLLOIDS.

Experiment 21.

Catalyzers.—Colloidal platinum and colloidal platinum + potassium cyanide or iodine.

Reaction Catalyzed.—$2H_2O_2 = 2H_2O + O_2$.

Preparation of the Experiment.—Prepare some colloidal platinum solution as follows:[1] Attach each of two short platinum wires 1 mm. in diameter, to a stout copper wire, covered with insulating material, by binding the ends of the copper and platinum wire together with thin copper wire. Slip a small glass tube over each platinum wire so as to cover it within 1 cm. of its free end. Connect the wires with the terminals of a 110-volt-direct-circuit, having a 32-candle-power lamp in series. Place pure distilled water, best that distilled from alkaline permanganate, in a crystallizing dish 10 cm. in diameter, and surround this dish, in a larger one, with cracked ice and water. Grasp the glass tubes firmly in the hand, bring the two platinum points together beneath the surface of the pure water, and immediately separate them so as to form an arc. Maintain this arc for about ten minutes, pulling the platinum points apart when they fuse together and touching them momentarily when the arc disappears as a result of too great separation of the wires. Filter the black solution thus obtained and keep it in a stoppered bottle. Place in each of two lecture test-tubes 25 cc. of hydrogen peroxide made slightly alkaline with ammonium hydroxide. Provide 2 cc. saturated potassium cyanide solution, 2 cc. 5 per cent. solution of iodine in potassium iodide, two 10 cc. graduates, and a medicine dropper.

Experiment.—Measure out two 10 cc. portions of the colloidal platinum solution, and add to one portion about 5 drops of the

[1] According to Bredig's directions. See *Ztschr. phys. Chem.*, 31, 271 (1900).

potassium cyanide solution. Pour one of these two portions into each of the tubes of hydrogen peroxide. After a vigorous effervescence has started in the solution which contains no cyanide, add about 5 drops of the iodine solution to it.

Observations.—After the hydrogen peroxide has stood about a minute with the colloidal platinum solution, a vigorous effervescence occurs in the solution which contains no potassium cyanide, while in the solution in which the cyanide is present no appreciable evolution of gas occurs. Immediately after adding the iodine to the effervescing tube, the reaction slackens, and in the course of a few seconds the evolution of oxygen almost entirely ceases.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

[CONTRIBUTIONS FROM THE LABORATORY OF THE BUREAU OF CHEMISTRY No. 44. SENT BY H. W. WILEY.]

THE POLARIZATION OF FRUITS, JELLIES, JAMS, AND HONIES.

BY L. M. TOLMAN.

Received March 8, 1902.

LARGE amounts of sucrose are added in the preparation of jellies and jams, some of which is inverted in the process by the action of the organic acids, such as citric, malic, or tartaric. As a rule the jams which are cooked the longest[1] show the largest amount of inversion as would be expected. In working with a large number of these products, however, the rather curious fact was noted that apparently complete inversion rarely if ever took place, or, at least, in polarizing before and after inversion there was always an increase in the minus reading on the sugar scale, often not more than from 1° to 2°, which calculated as sugar by the Clerget formula showed from 1 to 1.5 per cent. of cane sugar. The usual explanation of the phenomenon is that it is due to cane sugar, but it is probable that this change is due to an entirely different cause.

It must be remembered that the cane sugar in these products has been inverted by the action of the fruit acids and it is possible

[1] Tolman, Munson, and Bigelow: This Journal, **22**, 351 (1901).

to show by some investigations made by myself recently that this change in polarization is due to the action of hydrochloric acid on the invert sugar present. What this action is has never been explained, but it is a well-known fact that the simple presence[1] of hydrochloric acid increases the rotatory power of invert sugar. This is shown in the following table from Lippmann[2] in which is noted the effect on the polarization of an invert sugar solution at 20°, of different amounts of hydrochloric acid.

TABLE I.

Weight of sugar Grams.	Polarization Ventzke degrees.			
	5 cc. HCl.	10 cc. HCl.	15 cc. HCl.	20 cc. HCl.
26.048	−34.00	−35.04	−35.95	−36.80
13.024	−33.00	−34.12	−35.15	−36.03

Lippmann's polarizations were all made at 20° C., and in the case of the half-normal weight the reading was multiplied by 2 for comparison. This table shows that hydrochloric acid, by its simple presence, affects the polarization. It is but logical to suppose that, if each succeeding 5 cc. of the hydrochloric acid affected the polarization, the first 5 cc. must also, and that if an inversion were made without any acid present the reading would be still less.

In order to demonstrate this fact, *i. e.*, that an addition of hydrochloric acid increases the rotation of invert sugar, especially with regard to such invert sugar as has been prepared with organic fruit acids, and honey in which the sugar has perhaps been inverted in the digestive tract of the bee, and to justify the expectation that in making a polarization, before and after inversion, with these substances a change in reading of 1° or 2° would take place even when no sucrose was present, the following experiment was undertaken.

(It might be well to say in the beginning that all the polarizations were made in a water-jacketed tube and in that way the temperature was very exactly controlled. In most of the polarizations the greatest change in temperature was not more than 0.2° C., and correction was made for that difference.)

A strong solution of cane sugar was taken and inverted with citric acid (2 grams to 100 cc.) by boiling for one-half hour.

[1] H. A. Weber: This Journal, 17, 321, et seq.
[2] Lippmann: "Chemie die Zuckerarten," p. 800.

Fifty cc. portions were measured into 100 cc. flasks and each test was run in a duplicate, the average of a number of readings being taken.

One set of 2 flasks was made up to volume with distilled water. To another set 5 cc. of hydrochloric acid (sp. gr. 1.20) was added, the volume made up to 75 cc. and heated to 67° C., in fifteen minutes, according to the directions for the inversion of cane sugar used by the Association of Official Agricultural Chemists. To a third set 10 cc. of hydrochloric acid were added and treated as in the previous case. To a fourth and fifth set 5 and 10 cc. of hydrochloric acid were added and they were at once made up to volume in the cold and polarized, giving the acid practically no chance to exert any inverting action.

The second and third sets were cooled, made up to volume, and polarized. The results obtained are shown in Table II.

TABLE II.

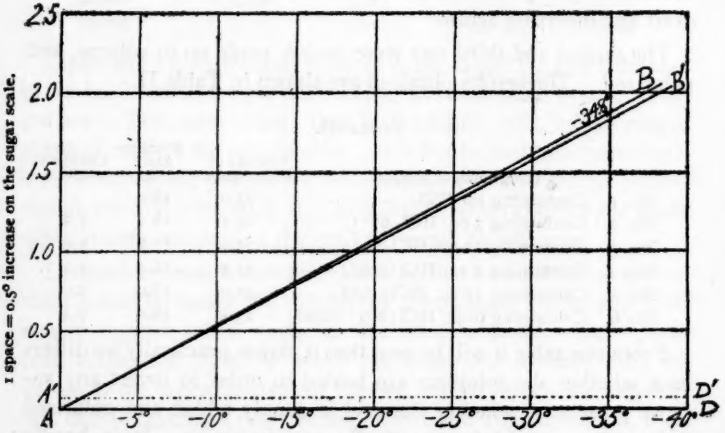
Description of sample.	Ventzke 0°. Polarization	Temperature. °C.	Change in rotation.
No. 1. Containing no HCl.....	— 23.0	18.0	..
No. 2. Containing 5 cc. HCl, 67° C.....	— 24.2	18.4	1.2
No. 3. Containing 10 cc. HCl, 67° C.....	— 25.0	17.8	2.0
No. 4. Containing 5 cc. HCl (cold)	— 24.2	18.4	1.2
No. 5. Containing 10 cc. HCl (cold)	— 25.0	18.0	2.0
No. 6. Containing 10 cc. HCl (N/4) (cold)	— 23.4	18.0	0.4

From this table it will be seen that it makes practically no difference whether the solutions are heated in order to invert any sucrose present or whether the acid is simply added and polarized before there could be practically any inversion. It is hardly possible to say that there had been immediate inversion in the cold by the acid of a small amount of sucrose present to account for the change in rotation caused by the acid in the cold, as it is well known that hydrochloric acid inverts very slowly in the cold.

It seems evident enough that the presence of hydrochloric acid increases the levo-rotatory power of invert sugar as shown in Table II, from the comparative effects of the 5 cc. and the 10 cc. of strong hydrochloric acid and of the weak N/4 hydrochloric acid.

This experiment is made under practically the same conditions as are present in jam in which the sucrose had been inverted with some fruit acid. The direct polarization is made, the hydrochloric

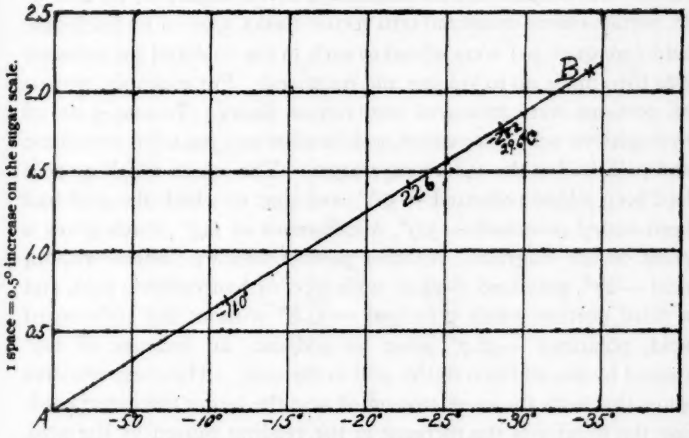
acid added to cause the inversion, and there is an increase of rotation to the left of from 1° to 2°, depending on the amount of invert sugar present and the amount of hydrochloric acid added. Calculated as cane sugar, this change amounts to from 1 to 1.5 per cent., whereas in reality there is no sucrose present and the change in rotation has been due to the causes explained above. The same conditions are present in honey in which there is a large amount of invert sugar. But even in case the inversion has been effected by hydrochloric acid and this acid is still present, the simple addition of more hydrochloric acid, as is shown in Tables I and II, causes an increased rotation. For these reasons it is not possible



Each space equals 5° on sugar scale, Schmidt and Haensch polariscope. B′ is calculated from Herzfeld's formula. 5 cc. HCl used in 100 cc. German official method.

Fig. 1.

to make any accurate determination, by polarization, before and after inversion, and the calculation by the Clerget formula, of a small amount of cane sugar in the presence of a large amount of invert sugar, unless a correction can be introduced to compensate for this action. The writer has endeavored to construct a formula which would correct this error. In order to show clearly the basis of the proposed correction, it is necessary to consider first Figs. 1 and 2 and the Herzfeld formula.



Each space = 5° on sugar scale of Schmidt and Haensch polariscope. 10 cc. HCl in 110 cc. Method of Association of Official Agricultural Chemists.

Fig. 2.

Fig. 1 shows graphically the effect of the hydrochloric acid used in inversion in the German method, in which 5 cc. is added to the solution to be inverted, the volume made up to 75 cc. and inverted by heating to 67° C. in fifteen minutes and cooled rapidly, after which the volume is increased to 100 cc. and the solution is polarized. The abscissas give the polariscopic readings of the solution of invert sugar in number of degrees to the left, and the ordinates give the increase in tenths of degrees that the addition of 5 cc. of hydrochloric acid causes.

Since the reading of the invert sugar before and after adding the hydrochloric acid was all that was needed in order to plot the diagram, two solutions of invert sugar were prepared: One by inversion with citric acid (2 grams to 100 cc.) and the other by use of N/5 sulphuric acid and the acid removed by the use of barium carbonate, which gives a solution of invert sugar free from any substances which might affect its optical action. Neither of these solutions was of a definite strength. Parallel experiments were carried on, using the two solutions; but the results as plotted in Fig. 1 were identical. The procedure in all of the following experiments was the same except for the varying amounts of hydro-

chloric acid added. Of the solution of invert sugar, 10, 15, and 50 cc. portions were measured into 100 cc. flasks, 5 cc. of hydrochloric acid (sp. gr. 1.20) were added to each in the cold and the solution was then made up to volume and polarized. For example, two 10 cc. portions were measured into 100 cc. flasks. To one, 5 cc. of hydrochloric acid were added, and the other was made up to volume and polarized at the same temperature. The one to which no acid had been added polarized —5.6°, and that to which the acid had been added polarized —5.9°, a difference of 0.3° which gives a point on the diagram. Another portion which polarized without acid —23°, polarized —24.2° with 5 cc. of hydrochloric acid, and a third portion which polarized —34.8° without the addition of acid, polarized —36.7° after its addition, an increase of 1.9° caused by the addition of the acid in the cold. These experiments show that with the same amount of acid the larger the invert reading the greater is the increase in the reading caused by the acid. Fig. 1 illustrates this point and from it one can easily determine in any particular case, as for instance, in polarizing a jam which reads —19.5° before inversion and —20.5° after inversion, that the change is not due to any sucrose present but is the change to be expected from the action of the acid. By examining the diagram it will be seen that 5 cc. of hydrochloric acid causes an increase of —1.05° in reading in a solution that polarizes —19.5° thus making the reading —20.55°. Any one who has polarized honey to any extent has noticed this slight change. In Table III, I have noted a number of polarizations of honies taken from U. S. Dept. of Agr., Div. of Chem., Bull. 13, and have corrected them from Fig. 2, which shows the effect of the amount of acid used in the method of the Association of Official Agricultural Chemists in which the larger amount of acid used (10 cc. in 110 cc., or nearly twice that used in the German method) causes a greater increase in the minus reading. The calculated minus readings are obtained by adding to the direct reading the correction for the effect of the acid as calculated from Fig. 2.

TABLE III.—POLARIZATION OF HONIES.

Direct.	Invert.	Degrees Ventzke. Cane sugar.[1]	Degrees Ventzke. Calculated invert reading.
— 20.00	— 20.90	0.72	— 21.25
— 17.60	— 18.32	0.93	— 18.59
— 16.8	— 18.40	1.23	— 18.20
— 15.8	— 17.5	1.31	— 16.78
— 11.0	— 12.0	...	— 11.68
— 13.2	— 15.6	...	— 14.00
— 16.50	— 18.00	...	— 17.52
— 14.80	— 15.60	...	— 15.70
— 9.40	— 10.67	0.96	— 9.98
— 12.90	— 13.86	0.73	— 13.70
— 14.40	— 15.40	0.76	— 15.39
— 11.30	— 12.65	0.99	— 12.00
— 11.50	— 12.65	0.85	— 12.21
— 13.50	— 14.00	0.30	— 14.33
— 9.5	— 10.00	0.30	— 10.05
— 11.0	— 12.00	0.70	— 11.68
— 10.0	— 11.00	0.70	— 10.62
— 11.0	— 12.00	0.70	— 11.68

Using the Herzfeld formula,[2]

$$S = \frac{a - b}{141.85 + 0.05\,b - \frac{T}{2}},$$

S = Sucrose.
a = Direct reading.
b = Invert reading.
T = Temperature,

in which 141.85, the factor for 1 gram of sucrose in 100 cc., is increased by 0.05 of the invert reading, and plotting a line in the same way as has been previously explained in plotting the results, it will be found that the two lines almost exactly coincide (see Fig. 1). For instance, suppose a minus polarization of — 35° is multiplied by 0.05, giving 1.75°. As Herzfeld begins with a polarization of —1.3°, corresponding to 1 gram of sugar at 20°, we mark off on the line AB the point at which —1.3° would intersect it and draw $A'D'$ and use that as a base line. At 35° on this base line measure 1.75° and it will be found to be almost exactly on

[1] As calculated from direct and invert reading.
[2] Herzfeld: *Ztschr. Rübenzucker-Ind.*, **40**, 194.

the line *AB*, which bears out the results previously obtained and shows that the method by which they were obtained is correct. In order to determine the effect caused by 10 cc. of hydrochloric acid in 110 cc. of sugar solution (the amount of acid used in the A. O. A. C. method), it is necessary to fix one point in Fig. 2 very carefully and from that to draw a straight line to the origin and there is obtained at once the correction to be made in the Herzfeld formula in order to obtain a new formula which will be correct for this method. In Fig. 2 is shown the determination of this correction. From Fig. 2 it is seen that the increase due to 10 cc. of hydrochloric acid (sp. gr. 1.20) in 110 cc. is 0.062 times the invert reading, while in the Herzfeld formula it was 0.050 times the invert reading. Therefore in order to make a formula for the official method, we substitute 0.062 for 0.050, also changing the factor 141.85, for 1 gram of sugar, to 141.79, which is apparently the limiting case if one plots the line. Thus we obtain the formula

$$S = \frac{a - b}{141.79 + 0.062\,b - \frac{T}{2}}.$$

While this formula may be used for calculating the amount of sucrose present, for any concentration, from polarization before and after inversion, it does not, stated in this form, give a means for calculating small amounts of cane sugar in the presence of large amounts of invert sugar. In order to make this determination, a slightly different method of calculation must be pursued. As $(0.062 \times b)$ is equal to the effect of the acid, if this is subtracted from b, it will give the true polarization, thus,

$$S = \frac{a - (b - (0.062 \times b))}{141.79 - \frac{T}{2}}$$

Now if a and $(b - (0.062 \times b))$ are equal, it is evident that all the change in polarization has been due to the effect of the acid used in inversion on the invert sugar, while if there is still a difference the cane sugar can be calculated by the use of $141.79 - \frac{T}{2}$. This formula will not apply to fruit products containing glucose, but is of special value in estimating small amounts of cane sugar

in fruits, pure fruit jellies, jams, and honies in which large amounts of invert sugar are present.

The action of acid on invert sugar mixed with glucose is the same as it is on the same amount of invert sugar alone, as the following results show:

TABLE IV.

	Polarized. °Ventzke.	Temperature. °C.
13.028 grams invert sugar + 25 cc. glucose solution	+9.8	21.0
The same + 10 cc. hydrochloric acid.....	+8.9	21.0
The same + 5 cc. hydrochloric acid.....	+9.4	21.0

This shows that when glucose which contains invert sugar is polarized before and after inversion, there will be a change of polarization even if there is no sucrose present. This condition would be almost always found in honey adulterated with glucose. This obviously can not be corrected by the formula given, and the writer is working on the use of inverting agents, such as citric acid, which have practically no effect on the opticity of invert sugar.

These results show that if you eliminate the effect of the acid used in inversion, *the Clerget formula will become a constant for any given temperature regardless of the concentration of the sugar solution.* This can be seen by noting from Fig. 1 that the increase of invert reading caused by the hydrochloric acid is 0.05 of the invert reading, so that Herzfeld's formula would be

$$S = \frac{a - b}{141.85 - \frac{T}{2}},$$

if the effect of the acid was removed, or a constant at any temperature.

If an inverting agent could be obtained which had no effect on the invert sugar, the question of concentration would practically be eliminated. But the elimination of this error would necessitate the determination of a new factor which would in all probability be 141.79 or perhaps a little less.

From this work it will be seen that the smaller the amount of hydrochloric acid used, the less is the effect on the negative reading, and therefore the smaller the error due to concentration. It

will be seen from Table II that the effect of N/4 hydrochloric acid is comparatively small, and the factor for any given temperature approaches a constant for all concentrations. All will agree that this is a most desirable condition for attaining accuracy.

The German method of using ½ normal weight (13.024 grams) and 5 cc. of hydrochloric acid reduces the error, as compared with the A. O. A. C. method, due to concentration, to a considerable extent, for two reasons. The smaller amount of acid has less effect on the negative reading and it has been shown from Table II that the smaller the amount of sugar used the less is the variation. As, for instance, the factor varies from 141.85 to 142.66, for 1 gram to 13 grams of sugar, a variation of 0.81°, and with the A. O. A. C. method it varies from 141.85 to 144.00, 2.1°.

The use of less acid for the inversion is desirable and it is in this direction that investigation should tend. The smaller the amount of the acid the less is the danger of destruction of the sugar and the smaller the error due to concentration, but it must be remembered that every change in the strength or amount of acid used requires the most careful determination of a new factor.

The work can be summed up in this way:

1. Hydrochloric acid increases levo-rotation of an invert sugar solution.

2. This increase, other things being equal, is proportional to the quantity of hydrochloric acid used.

3. Other things being equal and temperature varying, hydrochloric acid increases levo-rotation by a definite per cent. of the polarization.

4. In order to correctly calculate the percentage of cane sugar in invert sugar by Clerget's formula a correction depending on the amount of hydrochloric acid used must be made, which can be calculated from Fig. 1 or 2. All readings of the polariscope should be made at or about 20°.

THE SUBSTITUTION OF HYDROGEN FOR CHLORINE IN TRICHLORMETHYLPARACONIC ACID.

(SECOND PAPER.)

By Henry C. Myers.

Received February 22, 1902.

In the *Journal of the Chemical Society* for June, 1897, I called attention to some extremely unstable condensation products resulting from the reduction of dichlormethylparaconic acid in attempting to eliminate the remaining chlorine atoms. One compound being monochlordiparaconic acid, $C_9H_9ClO_2$, and another, also an acid, having the formula $C_9H_{12}O_2$. Secondary to other published work, I have continued these investigations.

Finding that the reduction of the dichlor acid by various agents was not in the direction of methylparaconic acid, which substance I hoped to reach by this method, I decided to treat the trichlor acid with sodium amalgam, the trichlor acid being readily prepared on condensation of chloral with sodium succinate in the presence of a suitable dehydrating agent.[1]

Trichlormethylparaconic acid was dissolved in water, treated with sodium hydroxide to retard the action of free acid, small pieces of solid sodium amalgam added occasionally and the cylinder surrounded with ice. Frequently during a two-days' treatment, sulphuric acid was added to prevent the solution becoming more than weakly alkaline. Eventually sulphuric acid was added in large excess and the mixture extracted with ether; on recrystallization from water the result was found to be an almost quantitative yield of the dichlor acid. This method, as regards the preparation of dichlormethylparaconic acid, is much simpler than the laborious process of reducing with zinc dust and acetic acid and finally precipitating with hydrogen sulphide as described by Miller (*Loc. cit.*), large amounts of zinc being precipitated completely only on repeated treatment with hydrogen sulphide, and filtration being extremely slow and unsatisfactory.

[1] Miller: *Ber. d. chem. Ges.*, **23**, R. 92 (1890); *Ann. Chem.* (Liebig), **255**, 43.

LONG-CONTINUED REDUCTION.

The above treatment with sodium amalgam when continued for a week or ten days resulted in three definite compounds, one of which has never been previously observed; (*a*) the dichlor acid with its characteristic properties and melting-point of 142°; (*b*) monochlordiparaconic acid of orange color and melting-point of 220°, obtained by recrystallization from alcohol; (*c*) a new acid in relatively small amounts with melting-point of 126°-127° and found in the final ether extraction as follows: On completion of the treatment with sodium amalgam the solution was acidified with hydrochloric acid. The monochlordiparaconic acid being insoluble in water formed an extremely voluminous precipitate which was filtered off and recrystallized from alcohol. The filtrate on extraction with ether yields the white crystalline dichlor acid, readily purified by crystallization from water. Repeated extraction with ether gives a yellowish oil which on long standing over sulphuric acid forms well defined crystals. These on being recrystallized from water and washed with ether have a constant melting-point of 126°-127°, resemble benzoic acid in appearance, do not decompose on standing for a year, are soluble in sodium carbonate solution, acid to litmus, and do not decompose on repeated melting.

BEHAVIOR OF MONOCHLORDIPARACONIC ACID TOWARDS HEAT.

In making melting-point determinations of this acid in the usual way, with capillary tube and paraffin-bath, it was noticed that the acid on melting underwent decomposition giving off a gas in small bubbles. In order to observe the change more closely, a long slender test-tube was substituted and considerable material used. In this way it could be observed that the substance really began its decomposition at about 190°, giving off fumes of hydrochloric acid and depositing white needle-like crystals on the tube just above the paraffin. I doubt if the true conditions of melting-points so called, can be observed in minute capillary tubes. These observations resulted in my placing about 3 grams of material in a U-tube heating the same as high as 226°, meanwhile drawing air through the apparatus. The air was previously freed of moisture and carbon dioxide; the products of the change were drawn

through calcium chloride, silver nitrate and caustic potash. Sublimation began at 181° followed by an effervescence of gas at 190°. The following figures show the total loss in weight in the U-tube and the corresponding increase in weight in each of the receiving tubes:

	Gram.
Loss in U-tube	0.6097
Gain in calcium chloride tube	0.0369
Gain in caustic potash tube	0.0662
Gain in silver nitrate tube	0.4854

CALCULATED LOSS CORRESPONDING TO 1 MOLECULE OF EACH GAS USING 2.9470 GRAMS OF MATERIAL.

	Calculated.	Found.
Hydrochloric acid gas	0.5830	0.4854
Water	0.2875	0.0369
Carbon dioxide	0.7028	0.0662
		0.5885

As the weights of water and carbon dioxide are too low for the loss of a single molecule and the total gain corresponds almost exactly with the loss of a single molecule of hydrochloric acid (calculated 0.5830, found 0.5885) I assume that the change is represented by the following reaction:

$$C_9H_9ClO_2 = HCl + C_9H_8O_2,$$

and that the increase in weight in the calcium chloride and caustic potash tubes were due to hydrochloric acid alone.

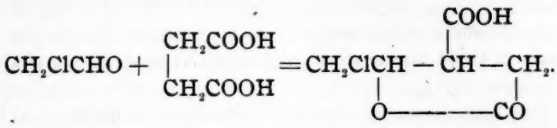
CONCLUSION.

Trichlormethylparaconic acid on reduction with either zinc dust or sodium amalgam in the presence of acids produces the dichlor acid in almost quantitative amounts, except where treatment is long continued with the amalgam. In the latter case, three distinct and well defined acids result; *viz.*, Dichlormethylparaconic acid, monochlordiparaconic acid, and a new acid with melting-point at 126°-127°. The dichlor acid on reduction produces monochlordiparaconic acid, according to the following equation:[1]

$$2C_6H_6O_4Cl_2 = C_9H_9O_2Cl + 3HCl + 3CO_2.$$

[1] *J. Chem. Soc.*, June, 1897.

Monochlordiparaconic acid on reduction forms an acid, $C_9H_{12}O_2$, which I found too unstable for investigation. Considering that these reductions do not lead in the direction of methylparaconic acid and that aldehyde as well as chloral condenses with sodium succinate in the presence of dehydrating agents, it would be of interest to treat similarly the monochlor aldehyde. Possibly the following change might result:



This monochlormethylparaconic acid, which I believe has never been prepared, might reduce to methylparaconic acid and yet the tendency of these compounds seems to be to double the molecular weight on giving up chlorine. On account of the extreme complexity of these changes and the instability of resulting compounds, as well as the great length of time necessary to prepare material, very little progress can be made unless one is willing to devote a year to the queston as it now stands.

UNIVERSITY OF CALIFORNIA.

[CONTRIBUTION FROM THE NORTH CAROLINA EXPERIMENT STATION.]

NITRIFICATION IN DIFFERENT SOILS.[1]

BY W. A. WITHERS AND G. S. FRAPS.

Received February 22, 1902.

IN a previous article[2] the authors communicated some work on the rate of nitrification of some fertilizers in a pasture soil, in which it was found that the percentages of nitrogen in them nitrified in a definite time corresponded with their availability as measured by vegetation tests, with one exception. This exception was ammonium sulphate, which was nitrified to a very small extent, although it has a high availability.

Inasmuch as the prevailing opinion in regard to the process of nitrification is that organic nitrogen is first converted into am-

[1] An account of this work was read before the Association of Official Agricultural Chemists in November, 1901.

[2] This Journal, **23**, 318 (1901).

monium salts, then into nitrites, then to nitrates, it seemed strange that ammonium sulphate should possess a low rate of nitrification. Results of experiments by other workers were cited, in one of which ammonium sulphate was nitrified to a greater extent than dried blood, in the other to a less extent.

The explanation we then put forward to account for the unexpected behavior of ammonium sulphate is as follows:

1. Ammonium sulphate may hinder the action of the nitrifying organisms. This explanation does not account for the beneficial action of calcium carbonate.

2. The nitric and sulphuric acids formed by the action of the nitrifying organisms are detrimental to them, being neutralized only in part by the bases of the soil. This does not explain why a soil should nitrify dried blood more rapidly than ammonium sulphate, even when calcium carbonate is added.

3. Different soils contain different nitrifying organisms, some of which convert organic matter directly to nitrites, while others change ammonium salts to nitrites more readily.

All three of the above causes may be in operation. The work to be described is a continuation of that mentioned above, and was designed to test the hypotheses then put forward.

PLAN OF WORK.

The work was confined to a study of the comparative rate of nitrification of ammonium sulphate and cottonseed meal in different soils, both with and without the addition of calcium carbonate. The soils were obtained from different sections of the country and varied widely in their composition and properties.

The procedure was that described in the paper already referred to. The sample of soil was sifted through a coarse sieve, and the quantity of cottonseed meal or ammonium sulphate, containing 0.3 gram nitrogen, was intimately mixed with 500 grams of it. In some cases, additional tests were made with half this quantity of nitrogen. The mixture was placed in precipitating jars, and kept in a dark closet. When calcium carbonate was added, the amount taken was exactly sufficient to neutralize all the nitric and sulphuric acids which would be produced if the ammonium sulphate were completely nitrified. The same quantity was used for the cottonseed

meal. The amount of water in the soils was about 15 per cent.; at suitable periods, one or more jars in each set was weighed, and the estimated loss of moisture was replaced in all the jars. At the end of three weeks (a little longer in some cases), the nitrates were leached out, and determined by the Tiemann-Schulze method, correction being made for the nitrates formed in the soil to which no fertilizer had been added.

DESCRIPTION OF SOILS.

1667. Pasture soil from the farm of this college. A light loam, containing humus and not acid to litmus.

1668. Heavy clay soil from college farm. Contains very little humus, possesses low fertility, and is slightly acid to litmus.

1669. Black garden soil from Florida Experiment Station. Contains much humus and is acid to litmus.

1670. Soil from the Massachusetts Hatch Experiment Station. This soil is from a plot in field C, fertilized with ammonium sulphate, muriate of potash, dissolved bone-black, and stable manure since 1891. This is the plot giving the least satisfactory growth, especially upon lettuce, beets, spinach and onions. It contained little humus and was acid to litmus.

1674. Soil from Rhode Island Experiment Station, used in plot experiments. Slightly acid to litmus, contains humus.

1675. Sandy soil from the Red Springs test farm of the North Carolina Department of Agriculture. Contains little humus.

1676. Soil from plot 23, Rhode Island Experiment Station, fertilized with ammonium sulphate. This soil, and also 1677, 1678, and 1679, is from a series of plots which have been in use for some time to test the effect of lime on an acid upland soil.

1677. Soil from plot 25, fertilized with ammonium sulphate and lime.

1678. Soil from plot 27, fertilized with sodium nitrate.

1679. Soil from plot 29, fertilized with sodium nitrate and lime.

1680. Sandy soil from Tarboro test farm of the North Carolina Department of Agriculture.

Acknowledgment is hereby made to Director H. J. Wheeler, of Rhode Island, Chemist H. K. Miller, of Florida, Agriculturalist W. P. Brooks, of Massachusetts, and State Chemist B. W. Kil-

gore, of North Carolina, for their kindness in furnishing samples of soil.

EXTENT OF NITRIFICATION.

The table contains the result of the nitrification tests, expressed in percentage of the total nitrogen nitrified. It also gives the temperature and the water content of the soils.

Tests were made, with lead acetate paper, to see if any hydrogen sulphide was evolved during the nitrification. The soil extract was also examined. The results were negative.

NITRIFICATION IN SOILS.

		Average moisture. Per cent.	Temperature. Extremes. °C	Temperature. Mean. °C.	Per cent. nitrified. Alone.	Per cent. nitrified. With $CaCO_3$.
1667.	Ammonium sulphate	10.5	25–30	27	7.2	57.2
	Cottonseed meal.....	...	...	..	32.4	43.6
	½ ammonium sulphate..	...	...	..	...	71.8
	½ cottonseed meal	...	...	..	...	43.0
	Ammonium sulphate and cottonseed meal.....	...	...	..	...	22.3
1668.	Ammonium sulphate	13.0	25–30	27	0.6	11.6
	Cottonseed meal.....	...	...	..	0.0	—1.1
	½ ammonium sulphate ..	...	...	..	...	43 2
1669.	Ammonium sulphate	13.0	25–30	27	0.2	15.8
	Cottonseed meal.....	...	...	..	17.3	41.5
1670.	Ammonium sulphate	15.0	23–28	26	2.2	45.7
	Cottonseed meal.....	...	...	..	14.8	32.6
	Ammonium sulphate and cottonseed meal.....	...	...	..	0.5	...
1674.	Ammonium sulphate	10.7	20–26	22	2.1	2.3
	Cottonseed meal.....	...	...	..	3.4	4.9
	½ ammonium sulphate..	...	...	..	...	16.5
	½ cottonseed meal.....	...	...	..	...	10.9
	Ammonium sulphate and cottonseed meal.....	...	...	..	1.3	...
1675.	Ammonium sulphate	8.0	19–24	20	0.0	0.0
	Cottonseed meal.....	...	...	..	0.0	0.0
1676.	Ammonium sulphate	12.2	18–23	19	0.0	1.5
	Cottonseed meal.....	...	...	..	1.9	—1.3
	½ ammonium sulphate..	...	...	..	..	1.5
	½ cottonseed meal	...	...	..	..	0.6

		Average moisture. Per cent.	Temperature. Extremes. °C.	Temperature. Mean. °C.	Per cent. nitrified. Alone.	Per cent. nitrified. With $CaCO_3$.
1677.	Ammonium sulphate	11.7	18–23	19	1.0	5.6
	Cottonseed meal.....	...	...	..	1.8	6.2
1678.	Ammonium sulphate	12.1	18–23	19	0.0	0.6
	Cottonseed meal.....	...	...	..	0.0	0.0
1679.	Ammonium sulphate	12.5	18–23	19	1.2	3.0
	Cottonseed meal.....	...	...	..	2.9	10.6
1680.	Ammonium sulphate	9.5	19–24	20	0.0	—1.3
	Cottonseed meal.....	...	...	..	1.3	—0.8
	½ ammonium sulphate ..	...	...	..	..	0.8
	½ cottonseed meal	...	...	..	..	4.5

DISCUSSION OF RESULTS.

Effect of Temperature.—The nitrification was much more active in the first four soils, in which the temperature was 23°-30° C., than in the others, in which the temperature was lower.

Effect of Calcium Carbonate.—The addition of calcium carbonate invariably caused increased nitrification, if any nitrification at all took place. For example, the increase was from 100 to 366, 100 to 240 with cottonseed meal, and 100 to 800, 100 to 2100 with ammonium sulphate. In some soils, nitrification did not occur when calcium carbonate was not added. Previous liming of the soil did not keep the calcium carbonate from being effective.

Effect of Previous Liming of the Soil.—Practically no nitrification occurred in the acid unlimed soils (1676 and 1678), even in presence of calcium carbonate, while the same soil previously limed (1677 and 1679) nitrified the fertilizers.

Effect of Previous Fertilizers.—A limed soil (1677) fertilized with ammonium sulphate for some years nitrifies ammonium sulphate much more readily than the same soil which had received sodium nitrate (1679).

Variation in the Nitrifying Power of Soils.—All our results on different soils are not comparable, since the nitrification did not all take place at the same temperature. But we can easily see, that while some soils nitrify ammonium sulphate to a greater extent in three weeks than cottonseed meal, there are others in which the reverse is the case.

Effect of Increasing Ration of Soil to Fertilizer.—This usually resulted in a slight increase in the quantity of nitrates formed, thus involving a very great increase in the percentage of nitrification.

EXPLANATION OF RESULTS.

We will now discuss the bearing of these results upon the explanations we have previously put forward.

1. Ammonium sulphate may hinder the action of the nitrifying organisms. Additional evidence in favor of this hypothesis is afforded by the fact that the process of nitrification is more rapid when the quantity of ammonium sulphate is reduced.

2. Detrimental action of the nitric and sulphuric acids. This is in accord with the fact that calcium carbonate was always beneficial. This explanation has been generally accepted for a long time.

3. Different soils contain different organisms. This is in accord with our observation that some soils nitrify ammonium sulphate more rapidly than cottonseed meal, and with others the reverse is true. This is exactly what was expected when the experiments were instituted.

THE NITRIFYING ORGANISMS.

Our third hypothesis seems to be in opposition to the prevailing opinion that organic matter must necessarily be converted into ammonia as the first stage in nitrification. It does not seem to be in opposition to the facts as recorded in the literature on this subject, however, so far as we have been able to find. Warington, Frankland, and Stutzer each found that the pure nitrous organism is capable of nitrifying organic nitrogen. Omelianski[1] disputes this, and says that pure cultures of nitrifying bacteria are incapable of nitrifying organic nitrogen, but it must be converted into ammonia first. He claims that the opposite conclusions reached by Frankland, Warington, and Stutzer and his associates were based upon inaccurate observations. But it is possible that the organisms are different.

But even if it is true that Omelianski is right, it does not neces-

[1] Experiment Station Record, **12**, 115 (1901), abs.

sarily follow that bacteria which nitrify organic nitrogen to nitrites do not exist. All the conditions under which the nitrous organisms have been isolated tend to eliminate such germs, the cultures always taking place in the presence of ammonium salts as a source of nitrogen, and organic nitrogen being excluded. Such a medium is unfavorable to the nitrate bacterium, also. The isolation of the bacteria which oxidize organic nitrogen must be conducted in a medium containing organic nitrogen, but not gelatine, since it has been found heretofore that species of bacteria separated by culture on gelatine do not nitrify at all.

SUMMARY.

1. Addition of calcium carbonate invariably accelerates the nitrification of cottonseed meal and ammonium sulphate, especially the latter.

2. In some soils a greater percentage of the nitrogen in ammonium sulphate is nitrified than that in cottonseed meal, and in other soils, the contrary is the case, even in the presence of calcium carbonate.

3. The factors which produce this result are probably as follows: *a*. The presence of the ammonium sulphate diminishes the activity of the nitrifying organisms; *b*. The acids produced also hinder them; *c*. Different soils contain different classes of organisms, some of which nitrify organic in preference to ammoniacal nitrogen.

4. We have found no evidence on record that organisms which nitrify organic nitrogen directly do not exist. The fact that they have not been isolated by present methods may be due to their elimination by the use of ammonium salts, on which they cannot feed, in the nutritive medium.

5. Liming acid soils is favorable to nitrification.

6. Continuous application of ammonium sulphate to a soil previously limed increases its power of nitrifying ammonium sulphate.

NEW APPARATUS IN WATER ANALYSIS.

By George Edward Thomas and Clarence A. Hall.

Received March 12, 1902.

It is the purpose of the writers of this paper to present some new forms of apparatus which have been devised for use in the Chemical Laboratory of the Filtration Testing Station in connection with the improvement of the water supply of the City of Philadelphia.

I.

The first apparatus described is used in the determination of the free and albuminoid ammonia, according to the method of Wanklyn, consisting of a battery of six stills as shown in Fig. 1.

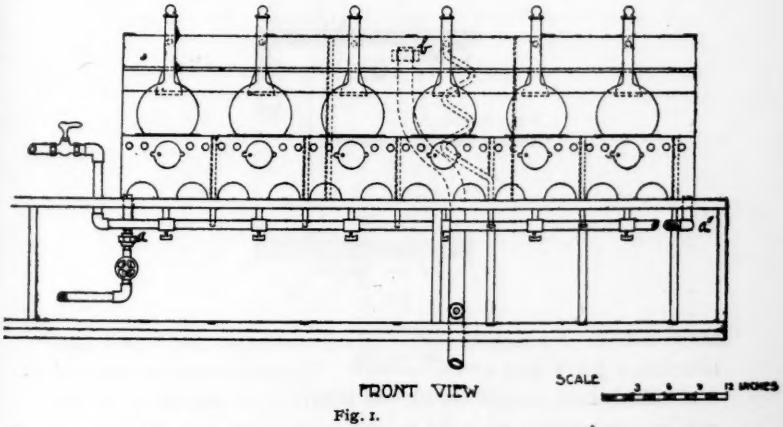


Fig. 1.

The flasks have side necks and ground glass stoppers, the capacity of the bulb being about 1800 cc. They are supported upon a burner shield constructed of galvanized sheet iron, the flasks resting upon wire gauze in holes 4⅜ inches in diameter. The burners are of a modified Fletcher type and are governed by individual cocks and a valve connected with the general supply. The flasks are united with the block tin worms by the side necks, which

are provided with rubber tubing—and extend into the tubes some distance beyond the point of contact of the rubber with the block tin (see Fig. 2), another piece of tubing overlapping this joint making a tight connection. The worms are ⅜ inch internal and ½ inch external diameter, coiled in a helix 2½ inch internal diameter with a 4½ inch pitch, being expanded at the entrance to

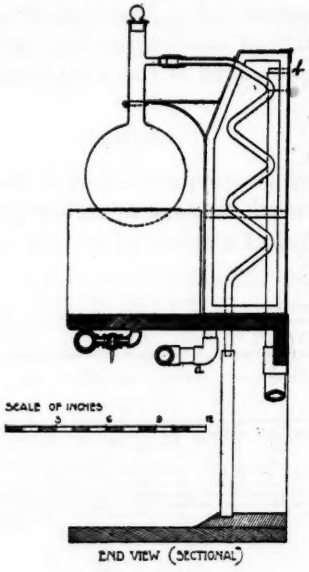


Fig. 2.

allow for the connection with the side necks of the flasks, and contracted for 1 inch at the outlets. The condenser is made of cold rolled sheet copper, 24 oz. per square foot, braced on the inside and provided with a lid hinged at the back and overlapping the front. The water is supplied at the extreme ends *a* and *a'* and overflows at the top *b* thus insuring thorough circulation. The whole system is supported upon a wooden shelf, allowing the operator ample space for handling the distillates, the Nessler tubes resting in sockets on a wooden slab upon the table. The salient features of this apparatus appear in its compactness, the manner

of connecting the flasks with the tin condensing worms, and the ground glass stoppers avoiding disconnection with the condensing tubes for the introduction of the alkaline permanganate prior to liberating the albuminoid ammonia.

Before making a determination, the system is cleansed by boiling off 50 cc. of distillate from 500 cc. of pure water rendered alkaline with sodium carbonate. 500 cc. of the sample are introduced and the determination made in the usual manner.

II.

The second apparatus to which attention is directed is shown in Fig. 3 and is used in collecting samples from reservoirs or rivers

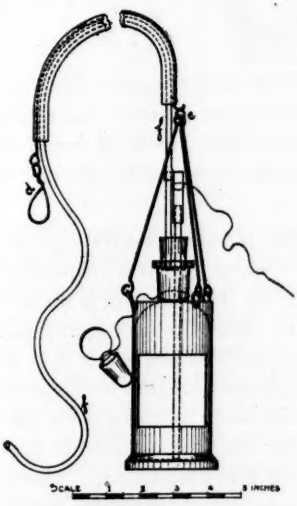


Fig. 3.

for the determination of the dissolved oxygen or carbon dioxide. It comprises a copper case, weighted at the base with sheet lead, holding securely a calibrated bottle of about 250 cc. capacity. This is supported by three copper wires joined at *c* and is suspended by the copper wire *d*. A glass tube passes through one of the holes of the rubber stopper nearly to the bottom of the bottle for the inlet of water; through the other a tube passes for the exit

of air; the former is supplied with a cap and the latter with rubber tubing which reaches to the surface. The wire *d* and the rubber tubing are surrounded by a ¼ inch rubber tube to prevent them from becoming entangled while the sample is being collected. The bottle is lowered until the required depth is reached, when the cap is removed by means of the string attached, allowing the water to enter. The apparatus is kept submerged until air is no longer expelled from the tube *f*, then the sample is raised to the surface, the wires disconnected and the rubber stopper removed, allowing the water remaining in the rubber tube *f* to fill the bottle to overflowing. The glass stopper attached is then inserted, the bottle taken from the case, the sample being ready for analysis.

III.

In the third division of our paper, a method is described for the determination of suspended matter. After an exhaustive study of various methods employed, we have found that the most satisfactory results can be obtained by filtering the water through asbestos.

Long fiber asbestos is soaked several days in a large quantity of clear (not distilled) water, which is frequently decanted and fresh portions are added. At the bottom of a Royal Meissen Gooch crucible, a layer of 3 mm. gravel is spread, this having been previously washed. A small quantity of asbestos is next placed on the gravel; it is necessary to separate the fibers by suspending it in water, as a good filter cannot be made by using a compact mass. After adding the asbestos, the crucible is placed to the lips and the bulk of the water held by the fibers blown out. There should now remain a perfect mat of asbestos covering the gravel and upon this the filter proper is constructed. More fiber is now added, in small portions, tapping the crucible lightly after each addition. When it is filled the forefinger is used to mold the asbestos around the sides of the crucible. The major portion of the water is now expelled by blowing, when the entire inner surface of the crucible should be covered with a compact asbestos lining. Any imperfections found in this surface necessitates reconstruction.

A perforated porcelain thimble is placed inside of the partially formed filter and more asbestos packed around the intervening space, nearly filling the crucible (see Fig. 4). Then the filter is

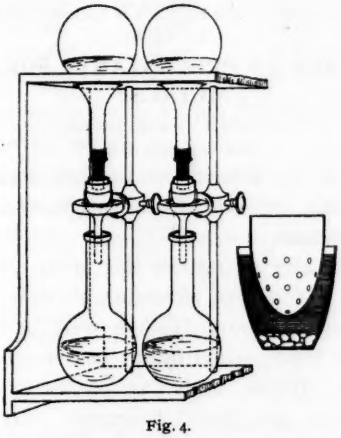


Fig. 4.

ready to be dried and weighed; it is necessary to heat for five hours at 110° C., in order to remove all the moisture, after which it is cooled in a desiccator and weighed rapidly, for the dissolved solids remaining in the filter may render it hygroscopic.

The method is to place the tared filter in the rack as indicated in the drawing, and to supply from a liter flask 1000 cc. of the sample of water for the determination. Loss is prevented while inverting the flask by compressing the rubber tubing at the neck, and by making use of the principle of the pneumatic trough the sample is fed automatically, part of the filtrate being used to wash down the particles adhering to the sides of the flask, again inverting and collecting the same upon the filter.

The crucible containing the suspended matter is dried and weighed under the same conditions as when prepared for use, the difference in weight representing the solid matter in suspension. In working with water carrying an unknown amount of dissolved solids the filter is first washed with some of that water and tared. This form of filter may be used repeatedly before it becomes inefficient, and it has been found convenient to use a battery of six units.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 62.]

AROMATIC BASES AS PRECIPITANTS FOR RARE EARTH METALS.[1]

BY ALICE MACMICHAEL JEFFERSON.

Received February 22, 1902.

THE purpose of the present investigation was to ascertain to what degree certain well-defined aromatic bases might be applied in metal precipitations.

It seemed advisable to restrict this study to the rare earth metals. To this end salts of zirconium, thorium, cerium, lanthanum, neodymium and praseodymium were selected, and these were acted upon in succession by the bases—aniline, *o*-toluidine, xylidine, dimethyl aniline, diethyl aniline, benzylamine, pyridine, piperidine, quinoline and phenyl hydrazine. Knowing the action of the mother base—ammonia—it was of interest to discover to what degree substituted ammonias and kindred bodies might affect the salts chosen for the study. The hope was also cherished that if differences in behavior with the proposed reagents were disclosed, perhaps separations of some of the metals might possibly be realized. It will be generally admitted that the probability of discovering such results would truly warrant a study such as has been indicated in the preceding lines.

I. ZIRCONIUM.

Solutions of zirconium nitrates were prepared with great care and used in the experiments about to be described.

Zirconium and Aniline.—A definite amount of the zirconium salt solution was removed by means of a pipette, and diluted to about 50 cc. To this, aniline was added and the liquid thoroughly agitated. A beautiful white, gelatinous precipitate separated almost immediately. It was allowed to stand over night and in the morning it was filtered, washed, dried, ignited and weighed. The results indicate that the reaction took place quantitatively.

[1] From author's thesis for Ph.D., 1901.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1382	0.0738	39.13	39.36
II.	0.0841	0.0436	39.13	38.24
III.	0.1050	0.0486	34.13	34.13
IV.	0.0908	0.0399	32.27	32.38
V.	0.3479	0.1248	26.45	26.46

Throughout the work the zirconium dioxide was ignited with a blast-lamp to constant weight.

Zirconium and o-Toluidine.—*o*-Toluidine also reacted quantitatively, giving a white gelatinous precipitate very similar to that obtained with xylidine. It was allowed to stand twelve hours before filtering.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.15084	0.0463	22.90	22.64
II.	0.15084	0.0463	22.90	22.64

Zirconium and Xylidine.—Xylidine precipitated zirconium quantitatively from its salts. About 50 cc. of the same solution were placed in a small beaker and xylidine added drop by drop with constant stirring. A white gelatinous precipitate formed which remained in suspension for some time. After twelve hours it was filtered, ignited, washed and weighed as zirconium dioxide. The precipitate was filtered with comparative readiness.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0908	0.0397	32.27	32.25
II.	0.0908	0.0401	32.27	32.58
III.	0.3479	0.1245	26.45	26.39

Zirconium and Dimethyl Aniline.—Dimethyl aniline was added to a portion of the zirconium solution with constant stirring. A yellowish white precipitate began to form slowly, and increased upon standing. After it had stood twelve hours it was filtered, washed, ignited to constant weight and the results calculated. It was found advisable to use a filter-pump in order to minimize the time factor for the excess of the precipitant filtered very slowly. The filtrate had a pink tinge.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0908	0.0394	32.27	32.00
II.	0.3479	0.1248	26.45	26.46

Zirconium and Diethyl Aniline.—The precipitation was made exactly as with dimethyl aniline. The products were very similar in appearance. The reaction took place rather slowly, and it was found advantageous to stir the liquid from time to time. After twelve hours it was filtered using a suction-pump and at times a slight violet tinge was noticed in the filtrate.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1050	0.0494	34.13	34.65
II.	0.0908	0.0401	32.27	32.58
III.	0.3479	0.1251	26.45	26.52

Zirconium and Benzylamine.—Benzylamine precipitated zirconium solutions quantitatively. The mass separated in small white floccules, which after standing a short time were easily filtered, and finally estimated as zirconium dioxide.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2158	0.0863	29.68	29.50

Zirconium and Pyridine.—A definite amount of the zirconium solution was placed in a small beaker, diluted to about 50 cc., and pyridine added with constant stirring. A very beautiful white glistening precipitate formed which settled rapidly and filtered readily after standing about an hour. After washing it was allowed to dry, and finally ignited with a blast lamp to constant weight. The results were as follows:

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0841	0.0438	39.13	38.41
II.	0.1050	0.0490	34.13	34.36
III.	0.1050	0.0486	34.13	34.13
IV.	0.0908	0.0399	32.27	32.38
V.	0.1814	0.0743	30.17	30.21

Zirconium and Piperidine.—Piperidine also seemed to precipitate zirconium solutions quantitatively. The precipitate formed almost immediately upon agitation, and was gelatinous and beautifully white in color. As soon as it had settled it was filtered and ultimately weighed as zirconium dioxide, after being ignited with a blast-lamp to constant weight.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0691	0.0367	39.13	39.18
II.	0.1050	0.0497	34.13	34.90
III.	0.0908	0.0404	32.27	32.82
IV.	0.2436	0.0876	26.45	26.52
V.	0.3479	0.1245	26.45	26.39

Zirconium and Quinoline.—When the zirconium salt was treated with quinoline and thoroughly stirred, a white glistening rather flocculent precipitate formed, which remained suspended for some time intermingled with the excess of the precipitant without settling. It was allowed to stand over night, then was filtered and ignited as before. In this case also the results seemed to indicate that a quantitative reaction had taken place.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0841	0.0452	39.13	39.60
II.	0.1050	0.0497	34.13	34.90
III.	0.1508	0.0463	22.90	22.64
IV.	0.1508	0.0462	22.90	22.59

The action of diphenylamine—a very weak base—upon zirconium salts was not tried, and it was found that phenyl-hydrazine caused no precipitation in such solutions.

It will be observed that nine of the ten precipitants were basic enough to remove zirconium from its salts. None of the substituted anilines proved too feeble for this purpose, notwithstanding the presence in them of positive groups.

II. THORIUM.

Here as with zirconium it was found that a solution of the nitrate was best adapted for the work. It was accordingly prepared by several methods and carefully tested as to its purity.

Thorium and Aniline.—Aniline precipitates thorium salts quantitatively. The precipitate did not form at once, but after the solution had stood a short time a cloudiness appeared in the solution and gradually increased. The precipitate was always allowed to stand over night, and if by that time it had not separated out nicely after stirring, it was allowed to stand another twelve hours. The clear white gelatinous mass was then filtered, and ultimately determined as thorium dioxide. The results were as follows:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1354	0.0651	42.29	42.25
II.	0.1354	0.0662	42.29	42.96
III.	0.1083	0.0519	42.29	42.11
IV.	0.1605	0.0768	42.29	42.05

Thorium and o-Toluidine.—*o*-Toluidine, like the other reagents, at first gave no precipitate, but on standing a heavy white very gelatinous mass formed. After several days, when the precipitate appeared to have settled nicely, the liquid was filtered and the precipitate was ignited and weighed. The resulting thorium dioxide after heating to constant weight with a blast-lamp, gave the following percentages:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1212	0.0577	42.29	41.81
II.	0.3210	0.1535	42.29	42.07
III.	0.3318	0.1582	42.29	41.89

Thorium and Xylidine.—Xylidine with thorium salts also gave a heavy white gelatinous precipitate. The solution was diluted to not more than 50-75 cc. and xylidine added with constant stirring. The precipitate remained with the excess of the precipitant, but after standing several days it settled upon the bottom of the beaker, and was estimated as usual.

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0541	0.0257	42.29	41.69
II.	0.1134	0.0537	42.29	41.60
III.	0.1605	0.0774	42.29	42.37
IV.	0.1605	0.0768	42.29	42.05

Thorium and Dimethyl Aniline.—Considerable time elapsed before any precipitate formed. After several days no reaction seemed to have taken place, but at the expiration of a week or ten days a precipitate was noticed which was filtered and its quantity determined. When the reaction commenced the solution seemed to separate into two layers, one whitish and opaque, and the excess of the dimethyl aniline, being lighter in specific gravity, remaining on top. On stirring, however, a white, very gelatinous precipitate formed, which filtered very slowly, one drop at a time; therefore a suction pump was found to facilitate the reaction considerably. The results are as follows:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1605	0.0774	42.29	42.37
II.	0.1605	0.0777	42.29	42.54

Thorium and Diethyl Aniline.—Diethyl aniline seemed to react quantitatively with thorium salts, but the desired result was reached with difficulty. At first no precipitation took place. After standing some time a yellowish white voluminous precipitate separated out. The product seemed more or less dependent upon conditions such as temperature, concentration, etc. The most satisfactory results were obtained from 25-50 cc. of solution, and when the beaker was permitted to stand in a rather warm place. Usually no precipitate formed until the solution had stood several days, and for one determination it stood one whole week before filtering. The mass was extremely gelatinous and at times almost transparent. The results were:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1624	0.0796	42.29	43.05
II.	0.1083	0.0517	42.29	41.92
III.	0.1512	0.0725	42.29	42.11
IV.	0.1605	0.0761	42.29	41.66
V.	0.3318	0.1579	42.29	41.82

Thorium and Pyridine.—When pyridine was added to the thorium salt, for a few minutes no reaction took place, but after

standing a white gelatinous mass separated out, slightly less dense than that obtained with piperidine.

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1083	0.0525	42.29	42.57
II.	0.1512	0.0737	42.29	42.81
III.	0.0756	0.0366	42.29	42.52
IV.	0.1605	0.0767	42.29	41.99

Thorium and Piperidine.—Piperidine precipitated thorium salts immediately, giving a white voluminous mass which is very characteristic. It settled rapidly and was filtered almost immediately, washed, dried and ignited to white thorium dioxide, heating with the blast-lamp until a constant weight was obtained. The results were:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1083	0.0525	42.29	42.57
II.	0.1512	0.0728	42.29	42.29
III.	0.0756	0.0360	42.29	41.78
IV.	0.1605	0.0769	42.29	42.10
V.	0.4701	0.2270	42.29	42.33

Thorium and Quinoline.—Quinoline gave a glistening white semi-transparent precipitate. The reaction seemed complete after standing twenty-four hours. It filtered with much greater readiness than the substituted anilines. The determinations were as follows:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1083	0.0522	42.29	42.35
II.	0.1083	0.0510	42.29	41.37
III.	0.1605	0.0770	42.29	42.16

Benzylamine was not tried on account of lack of material.

Phenylhydrazine with thorium salts gave a canary-yellow flocculent precipitate readily soluble in excess.

Diphenylamine was not tried.

In all of the analyses of the thorium salts the volume of liquid never was greater than 100 cc. and usually not above 50 cc.

It will be observed that while thorium responds quantitatively

to the same bases to which zirconium responded, and while the results are quantitative in character, the time factor in many cases is so extended that the application of these precipitants offers nothing of advantage to the analyst either in the direction of completeness of precipitation or rapidity of reaction.

Zirconium and thorium represent a rather wide range in atomic weights (90-232), and as the second has probably acquired somewhat more of the acid nature, this may account for the sluggishness of its behavior with the bases which were applied to it. This led to the introduction of cerium in the study, being a member of the same Group IV of the Periodic System with zirconium and thorium, and standing midway as it were in atomic weight (140) between them. The behavior of the chosen bases upon its salts was awaited with deep interest. Here, too, it may be added, that the precipitates in thorium solutions are from their very nature and behavior definite double salts. None of them showed the usual appearance of thorium hydroxide.

III. CERIUM.

The salt used was a ceric ammonium nitrate, orange-red in color.

Cerium and Aniline.—A definite amount of the cerium double salt was weighed and dissolved in about 50 cc. of water, and aniline added with constant stirring. A white heavy flocculent precipitate formed almost immediately, and the liquid went through various changes in color, finally becoming nearly colorless. After standing an hour or two, the solution was filtered and the precipitate was washed, dried, ignited, and weighed as cerium dioxide, yellow to reddish yellow in color. Throughout the work, the cerium dioxide was ignited to constant weight with the blast-lamp before weighing, as directed under zirconium. The following results were obtained:

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.4134	0.1281	25.13	25.22
II.	0.3554	0.1089	25.13	24.93
III.	0.3973	0.1254	25.13	25.69
IV.	0.3637	0.1113	25.13	24.91
V.	0.1996	0.0622	25.13	25.35

Cerium and o-Toluidine.—A white flocculent precipitate was formed by adding *o*-toluidine to a solution of the cerium salt and thoroughly agitating. The mass settled nicely, and after standing several hours was filtered, washed and ignited.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.0785	0.0245	25.13	25.35
II.	0.1682	0.0513	25.13	24.82
III.	0.1210	0.0377	25.13	25.17

Cerium and Xylidine.—Xylidine gave a heavy white precipitate that remained suspended for some time. After stirring very thoroughly the beaker was set aside for several hours, then filtered, using a suction-pump, washed, ignited and weighed. As the results failed to show a concordance the reaction seems not to have taken place quantitatively.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2106	0.0483	25.13	18.66
II.	0.1890	0.0460	25.13	19.79
III.	0.2368	0.0447	25.13	15.36

Cerium and Dimethyl Aniline.—Cerium was precipitated with dimethyl aniline with constant stirring. A yellowish white precipitate formed and the liquid changed color rapidly, green, purple and finally nearly colorless. After standing a couple of hours it was filtered and weighed as cerium dioxide. The reaction was not quantitative, as the percentages obtained showed great variation, and the results were unsatisfactory.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1418	0.0312	25.13	17.91
II.	0.0899	0.0214	25.13	19.34
III.	0.0899	0.0151	25.13	13.66

Cerium and Diethyl Aniline.—Diethyl aniline gave a white flocculent precipitate which settled with comparative readiness, the solution becoming brown, green, purple, and finally colorless. After standing for two hours it was filtered using a suction-pump.

Cerium dioxide ultimately obtained was ignited to constant weight with the blast-lamp.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1785	0.0566	25.13	25.80
II.	0.0899	0.0273	25.13	24.68
III.	0.0899	0.0290	25.13	26.24
IV.	0.0899	0.0285	25.13	25.78

Cerium and Benzylamine.—When benzylamine was added to a cerium salt with constant stirring, a heavy flocculent precipitate formed, which rapidly changed in color, becoming brown and finally nearly black. The precipitate settled rapidly and was filtered after standing several hours without the use of a suction-pump.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1142	0.0345	25.13	24.59
II.	0.1192	0.0375	25.13	25.59

Cerium and Pyridine.—Pyridine gave a beautiful white glistening precipitate that settled rapidly and filtered quickly and easily. It was very gelatinous. The results were quantitative.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1932	0.0609	25.13	25.65
II.	0.1192	0.0372	25.13	25.39
III.	0.2488	0.0775	25.13	25.35

Cerium and Piperidine.—Piperidine also gave a white precipitate, and its physical properties closely resembled those observed in the precipitate obtained with pyridine. The quantitative results were:

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2005	0.0631	25.13	25.62
II.	0.2248	0.0695	25.13	25.16
III.	0.1156	0.0360	25.13	25.35
IV.	0.2011	0.0635	25.13	25.70

Cerium and Quinoline.—Quinoline seemed not to give a quantitative reaction. I thought at first that the variation in results might be due to the fact that the quinoline used contained brown substances and that the excess of the precipitant clung to the sides of the beaker and was very difficult to remove, even when a glass rod with a rubber cap was used. It was thought that perhaps some of the precipitate might be lost in this way, so an alcoholic wash was used, and also chloroform, which completely removed the excess of quinoline from the beaker, but the final results were unsatisfactory.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.5027	0.1058	25.13	17.13
II.	0.2898	0.0591	25.13	16.60
III.	0.1720	0.0354	25.13	16.74
IV.	0.1364	0.0337	25.13	20.09
V.	0.2306	0.0326	25.13	11.49

In Experiment IV alcohol was used, and chloroform in Experiment V.

Both phenylhydrazine and diphenylamine failed to precipitate cerium salts.

Strangely enough, several of the bases failed to yield quantitative results. With xylidine this may be due to the presence of the additional methyl group; perhaps, too, in dimethyl aniline, the accumulation of positive substituents is the cause of the failure in reaction; if so, why should not the same occur in the use of diethyl aniline where quantitative precipitation does take place? The slight basicity of diphenylamine explains its failure, but the lack of action in quinoline is not so readily comprehended.

A glance at the arrangement of the elements in the Periodic System shows that directly opposite—preceding cerium—as a member of Group III, appears lanthanum, while following cerium in Group V, are neodymium and praseodymium. Would their conduct with the selected bases bring to light any unobserved facts? Lanthanum following in its oxide the type R_2O_3—a type readily precipitated by ammonia—might perhaps shed some light on the behavior of cerium, and account for the variations observed

between it and its associates of Group IV. Therefore, it was next considered in the proposed study.

IV. LANTHANUM.

Two salts of lanthanum were used, the chloride and the double nitrate with ammonium.

Aniline *o*-toluidine and xylidine all failed to precipitate lanthanum salts. Dimethyl aniline also gave no reaction, and diethyl aniline after long standing gave a slight film at the point of contact, though no precipitate was discernible.

Lanthanum and Benzylamine.—Benzylamine gave with lanthanum salts, as with the metals previously tested, a heavy white flocculent precipitate. When the resulting oxide was ignited to constant weight, it gave the following percentages:

	Salt taken. Gram.	La_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1685	0.0741	37.94	37.50
II.	0.2051	0.0628	24.96	26.11

Lanthanum and Pyridine.—At first no precipitate formed, but after standing several days a very fine white precipitate separated. It was granular and shining in appearance, and like that obtained with praseodymium, clung very closely to the beaker, and was only removed with the greatest difficulty, and showed a tendency to run through the filter-paper.

The results were not quantitative.

Lanthanum and Piperidine.—Piperidine gave a white glistening gelatinous precipitate, similar in properties to that obtained by the same reagent with the metals already mentioned.

	Salt taken. Gram.	La_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1580	0.0705	37.94	38.04
II.	0.1713	0.0750	37.94	37.33
III.	0.2106	0.0937	37.94	37.94
IV.	0.3826	0.1141	24.96	25.43

Diphenylamine was not tried, and quinoline failed to show any reaction.

Phenylhydrazine gave a flocculent reddish brown precipitate which grew less on standing.

Only those bases having a decidedly basic nature—benzylamine and piperidine—seem capable of throwing out lanthanum completely. Eight of them apparently fail of this end, and in this behavior is found a hint as to what cerium might be expected to do. It accordingly became still more interesting to ascertain the deportment of praseodymium and neodymium in the indicated directions.

V. PRASEODYMIUM.

Two salts were used, $Pr(NO_3)_3.6H_2O$, and the doube nitrate $Pr(NO_3)_3.2NH_4NO_3.4H_2O$, both green in color.

Aniline and praseodymium appeared not to react, although the behavior was rather confusing. Tests were made, but no precipitate formed even after long standing, but later, when the tests were repeated, it was found that when the test-tube stood in a warm place, a slight precipitate did form, which on long standing again disappeared.

Neither *o*-toluidine nor xylidine gave evidence of any reaction with praseo-salts even after long standing. Dimethyl aniline gave no precipitate and diethyl aniline behaved in a similar manner, though after standing for a long time, a very slight film was noticed at the point of contact.

Praseodymium and Benzylamine.—Benzylamine gave a white flocculent precipitate, very voluminous which, like many of the preceding precipitates, filtered rapidly, after standing several hours. The resulting brown-black oxide, after ignition with the blast-lamp, gave the following:

	Salt taken. Gram.	Pr_4O_7 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1348	0.0520	32.57	32.20

Praseodymium and Pyridine.—When pyridine was first added, no reaction seemed to take place, but on standing, a fine white granular precipitate separated on the bottom of the beaker. It was filtered and estimated as usual. The precipitate clung closely to the sides of the beaker, and it was almost impossible to thor-

oughly remove it. One analysis was made, and the result was unsatisfactory.

Praseodymium and Piperidine.—Piperidine gave a white, glistening, gelatinous precipitate, with a slight greenish tinge. Its properties were very similar to the neodymium-piperidine precipitate. Like the latter, it was found best to dry the product simply in the air, because when heated on a metal drying cone over a Bunsen flame, the mass melted and ran through the filter, and partly disappeared. It was a quantitative reaction.

	Salt taken. Gram.	Pr_4O_7 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2014	0.0788	32.57	32.67
II.	0.0970	0.0380	32.57	32.68
III.	0.0979	0.0378	32.57	32.22

Quinoline gave no precipitate, and the action of diphenylamine was not tried. Phenylhydrazine gave a flocculent reddish brown precipitate, which on standing partly disappeared.

Comparison with the behavior of lanthanum reveals the fact that these two elements behave almost analogously with the bases brought in contact with them and vary in about the same degree from cerium.

VI. NEODYMIUM.

Neodymium and Aniline.—When aniline was added to a neodymium solution at first no reaction seemed to take place, but after the beaker had stood some time, a slight gelatinous precipitate separated, white in color. After several hours the liquid was filtered, and the resulting blue-brown sesquioxide weighed. The reaction was not quantitative.

	Salt taken. Gram.	Nd_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.09855	0.0139	32.57	12.06
II.	0.09855	0.0109	32.57	9.44
III.	0.09855	0.0236	32.57	20.48

o-Toluidine gave no precipitate. Xylidine after long standing gave a very slight yellowish white flocculent mass. Dimethyl ani-

line at first failed to react, but after some time had elapsed a faint film was noticed.

Diethyl aniline showed a slight precipitate, yellowish white in color, but the result obtained was far from quantitative.

Neodymium and Benzylamine.—Benzylamine gave a voluminous white precipitate, which separated in small beautiful floccules. The result was quantitative.

	Salt taken. Gram.	Nd_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1608	0.0611	32.57	32.50

Neodymium and Pyridine.—Pyridine after standing a short time gave a slight yellowish white precipitate. The reaction was incomplete.

Neodymium and Piperidine.—The neodymium salt was immediately precipitated, giving a glistening white product, with a faint violet tinge. It was very gelatinous, but readily filtered, and gave results closely corresponding to the theoretical. It was dried simply in the air, for when I attempted to dry it upon a stove-plate, using a metal cone, the precipitate melted and ran through the filter-paper.

	Salt taken. Gram.	Nd_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I	0.2912	0.1135	32.57	33.44
II.	0.0985	0.0378	32.57	32.78
III	0.1471	0.0436	25.36	25.35
IV.	0.1869	0.0557	25.36	25.47

Quinoline failed to react. No attempt was made to precipitate neodymium salts with diphenylamine. Phenylhydrazine gave a fine orange-red flocculent mass, which on standing appreciably decreased in bulk, finally disappearing almost entirely.

The behavior of praseodymium is here repeated. In almost every particular the representatives of Group V conduct themselves similarly, and manifest a decided relationship, from the present point of study, to lanthanum, whereas they differ markedly from cerium. May not the obvious conduct of cerium with the different precipitants enumerated in the preceding paragraphs, be

safely regarded as decided evidence of the true position of cerium in the periodic classification. Is not its deportment with these bases more in harmony with that of zirconium and thorium than with that of lanthanum, neodymium, and praseodymium? Its juxtaposition to the latter unquestionably explains why it is not precipitated by xylidine, dimethyl aniline and quinoline, with all of which its natural associates gave quantitative precipitations.

SEPARATIONS.

Having made the observation that many of the precipitations described were quantitative, and that other salts with the same reagents failed to react at all, the thought arose that probably separations could be made, and accordingly investigations along these lines were begun. The results of these attempts are given in the following pages. The field seems to be a large one, by no means exhausted, and the possibilities appear great.

I. Separation of Thorium and Neodymium by Quinoline.—A known amount of the thorium solution diluted to approximately 50 cc. was placed in a beaker, and a weighed quantity of the neodymium salt added. Quinoline was then added with constant stirring and the beaker set aside for twenty-four hours. It was then carefully filtered and washed thoroughly, the beaker containing the neodymium filtrate removed, and a fresh vessel substituted. The precipitate while still moist was dissolved in dilute hydrochloric acid or preferably dilute nitric acid, and the filter-paper washed thoroughly with water to remove the last traces of the acid solution. It was found advisable to use as little acid as possible to prevent the final dilution from being unnecessarily great.

The acid solution was next neutralized as nearly as possible with ammonia water. A little nicety in manipulation was required, because if too great an amount of ammonia were added, the metals would be precipitated, while, on the other hand, too large an excess of acid would retard the reprecipitation by quinoline, making the final results too low. Leaving the solution very slightly acid, quinoline was again added, and the liquid agitated. The reaction commenced almost immediately, and in every case it

was noticed that the reprecipitation gave a mass much more flocculent than that obtained by simply precipitating once.

After twenty-four hours, the solution was filtered, adding this filtrate to the first one, and the precipitate washed, dried, ignited with the blast lamp to constant weight, and determined as thorium dioxide. The reprecipitation was found necessary, because when the thorium was only precipitated once, the resulting oxide showed a very faint color of neodymium, whereas the thorium dioxide obtained by dissolving and reprecipitating was in every case pure and white without the slightest trace of the blue-brown oxide of neodymium.

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.15466	0.0751	42.29	42.67
II.	0.15466	0.0746	42.29	42.38
III.	0.1206	0.0581	42.29	42.33
IV.	0.15157	0.0734	42.29	42.55
V.	0.15157	0.0724	42.29	41.96
VI.	0.15157	0.0728	42.29	42.20
VII.	0.15157	0.0740	42.29	42.88

II. Separation of Zirconium and Neodymium by Quinoline.—The separation was carried out exactly as directed under thorium, but in each case the precipitate stood twelve hours instead of twenty-four hours. The same precautions were observed. The results are appended.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.14406	0.0595	30.30	30.47
II.	0.14406	0.0590	30.30	30.20
III.	0.14406	0.0582	30.30	29.78
IV.	0.10948	0.0448	30.30	30.14
V.	0.15084	0.0462	22.90	22.59
VI.	0.15084	0.0471	22.90	23.00

Here also, the resulting zirconium dioxide was white, not the slightest trace of the color of the neodymium oxide being perceptible, but the neodymium percentages were too high when determined by ammonia in the filtrate. In each of the separations described the resulting filtrates were precipitated with pure am-

monia, but in every case the resulting percentages were found to be somewhat too high when compared with the theoretical.

	Salt taken. Gram.	Nd_2O_3 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2092	0.0624	25.36	25.51
II.	0.1433	0.0435	25.36	25.96
III.	0.1291			
	Taken together	0.0837	25.36	26.19
IV.	0.1442			

Zirconium and ammonia, the resulting mean, used as the unit of comparison:

	Salt taken. Gram.	ZrO_2 found. Gram.	Found. Per cent.	Mean. Per cent.
I.	0.14406	0.0587	30.00	
II.	0.14406	0.0597	30.54	30.30
I.	0.15084	0.0468	22.87	
II.	0.15084	0.0469	22.93	22.90

III. Separation of Thorium and Lanthanum by Aniline.—The procedure was exactly as directed under quinoline, and both times the precipitate stood twenty-four hours before filtering. It was advantageous to allow the excess of the precipitant to filter through, and then wash the precipitate with water before dissolving in dilute nitric acid, because otherwise the organic material in solution rendered it darker in color, and it was more difficult to decide when the point of neutralization was being approached. As the oxides of thorium and lanthanum are both white, it was, of course, not possible to tell whether the final thorium dioxide contained a slight amount of lanthanum by the color, as was done with the blue-brown neodymium oxide. Therefore, endeavoring to make the results as accurate as possible, the weighed thorium dioxide, was in each case treated in the crucible with concentrated hydrochloric acid or nitric acid, and allowed to stand several hours.

As the lanthanum sesquioxide is soluble in acids, it should dissolve leaving the thorium dioxide. The acid solution was poured quickly into a small beaker and the precipitate of thorium dioxide washed into the beaker with water. If care be taken, no milkiness

will be noticed. The liquid was then filtered, the precipitate ignited to constant weight, and finally weighed as thorium dioxide. The filtrate which would contain the trace of lanthanum if present, was added to the first filtrate known to contain the lanthanum from the separation. The final results were as follows:

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.3210	0.1550	42.29	42.43
II.	0.3210	0.1552	42.29	42.49
III.	0.3210	0.1550	42.29	42.43
IV.	0.3210	0.1552	42.29	42.49
V.	0.3210	0.1554	42.29	42.54

IV. Separation of Zirconium and Lanthanum by Aniline.—The reaction was carried out exactly as directed under the separation of thorium and lanthanum by aniline, except that in each case the time factor was twelve hours instead of twenty-four. The resulting zirconium dioxide was treated with concentrated hydrochloric or nitric acid to dissolve out any trace of lanthanum.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.13458	0.0576	31.96	31.57
II.	0.2539	0.1034	30.13	30.04
III.	0.2539	0.1036	30.13	30.09
IV.	0.2539	0.1043	30.13	30.29

Zirconium and Ammonium Hydroxide.

	Salt taken. Gram.	ZrO_2 found. Gram.	Found. Per cent.	Mean. Per cent.
I.	0.2539	0.1040	30.21	
II.	0.2539	0.1034	30.04	30.13
I.	0.1345	0.0586	32.10	
II.	0.2045	0.0883	31.82	31.96

V. Separation of Thorium and Lanthanum by Quinoline.—A known number of cubic centimeters of the thorium solution, and a weighed quantity of the lanthanum salt, were placed in a small beaker, diluted to about 50-75 cc. and quinoline added, stirring the liquid very thoroughly. The subsequent operations were carried out in a manner quite similar to that described in the preceding

experiments. The precipitate was allowed to stand twenty-four hours each time. The final thorium dioxide obtained was treated with concentrated acid, to remove any lanthanum that might have been carried down by the thorium.

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.3318	0.1577	42.29	41.77
II.	0.3318	0.1592	42.29	42.16
III.	0.3318	0.1581	42.29	41.86
IV.	0.3318	0.1585	42.29	41.98
V.	0.3318	0.1582	42.29	41.89

VI. Separation of Cerium and Praseodymium by o-Toluidine.—After ascertaining the fact that *o*-toluidine precipitated cerium salts quantitatively, and with the salts of neodymium gave no reaction, I endeavored to separate the two, using this means. It was found by experiment that if the precipitate of cerium were dissolved in acid, it refused to be reprecipitated when, after neutralizing, an excess of the precipitant was again added. Consequently, *o*-toluidine was added only once, and no attempt was made to dissolve and reprecipitate.

The experiment was made, using from 50-75 cc. of solution, and allowing the precipitate to stand over night before filtering. The resulting cerium dioxide seemed rather darker in color than usual, which may have been due to a trace of praseodymium oxide, notwithstanding the fact that the weight of the cerium dioxide found agreed with the theoretical within the limit of experimental error.

	Salt taken. Gram.	CeO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.1750	0.0543	25.13	25.25

VII. Separation of Thorium and Praseodymium by Aniline.—The confusing behavior of praseodymium with aniline has already been mentioned. I am inclined to think that possibly conditions such as temperature, concentration, etc., influence it, because when a test-tube containing the two stood in a warm place, a slight precipitate formed, which was quite perceptible, but after standing for some time in the cold, it entirely disappeared. At another time aniline and praseodymium stood in contact for months, without

any precipitate separating out. Another thought is that perhaps even if the conditions were such as to allow a precipitate to form, possibly the small amount of acid present in the solution after dissolving the thorium precipitate in acid and almost neutralizing, would be sufficient to prevent any reaction between the two.

Accordingly, an attempt was made to separate thorium from praseodymium using aniline as the precipitant. The method was quite similar to that pursued in the foregoing separations, the precipitate being allowed to stand each time for twenty-four hours. The mass first obtained was dissolved in dilute nitric acid, carefully neutralized and reprecipitated. The thorium dioxide ultimately obtained was treated in the cold with concentrated nitric acid, allowing it to remain undisturbed for two hours, hoping in this way to remove the slight trace of color noticed. After filtering, washing and igniting, a *very* faint brownish tinge was always noticed. The weights corresponded quite well with the theoretical but at no time was the resulting thorium dioxide absolutely white. Even after treatment with nitric acid, the thorium dioxide showed a slight tinge of color, upon close examination.

	Salt taken. Gram.	ThO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.3318	0.1600	42.29	42.37
II.	0.3318	0.1592	42.29	42.16
III.	0.3318	0.1600	42.29	42.37
IV.	0.3318	0.1602	42.29	42.43

An attempt was made to separate zirconium and praseodymium using *o*-toluidine. Only one analysis was attempted, and the result was rather low, but near enough to indicate the probability of such a separation being made under proper conditions. The zirconium dioxide obtained was perfectly white in color.

VIII. Separation of Zirconium and Lanthanum by Xylidine.— As previousy stated, xylidine precipitates zirconium quantitatively, so an attempt was made to separate zirconium from lanthanum using it as the medium. Xylidine was added to the solution containing the two salts, with constant agitation. The precipitate formed almost immediately, but as a matter of precaution it was allowed to stand over night. In the morning it was filtered, al-

lowing the excess of xylidine to run through the filter, washing thoroughly with water, and then with 95 per cent. alcohol, till the brown color of the xylidine had disappeared and the precipitate and filter were clean and white. It was then again washed with water, dissolved in dilute nitric acid and almost neutralized with ammonium hydroxide, leaving the solution very slightly acid. After reprecipitating with xylidine it was allowed to stand twelve hours, and again filtered, finally estimating as zirconium dioxide. The resulting oxide was treated for two hours in the cold with concentrated nitric acid, then filtered and determined as usual.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2158	0.0864	29.69	29.52

Zirconium and Ammonia:

	Salt taken. Gram.	ZrO_2 found. Gram.	Found. Per cent.	Mean. Per cent.
I.	0.2158	0.0863	29.50	
II.	0.2158	0.0874	29.87	29.69

If nitric acid were added to dissolve the precipitate in the separation of lanthanum and zirconium by xylidine, without previously washing with alcohol, the excess of xylidine would combine with the nitric acid, giving an organic precipitate so dense that it would prevent one from seeing when the point of neutralization was approaching in the subsequent treatment with ammonium hydroxide, hence the advisability of using an alcoholic wash.

IX. Separation of Zirconium and Praseodymium by Xylidine.— An attempt was made to separate these two in a manner perfectly analogous to that just described. The resulting zirconium dioxide was light yellow in color, though the weight corresponded with that required.

	Salt taken. Gram.	ZrO_2 found. Gram.	Required. Per cent.	Found. Per cent.
I.	0.2158	0.0867	29.69	29.63

SUMMARY.

Six metals were acted upon by characteristic aromatic bases, when it was found that zirconium is precipitated quantitatively

by nearly all of them. Thorium is precipitated by aniline, *o*-toluidine, xylidine, diethyl aniline, dimethyl aniline, pyridine, piperidine and quinoline. Aniline *o*-toluidine, diethyl aniline, benzylamine, pyridine and piperidine are the only precipitants of cerium, while with lanthanum, neodymium and praseodymium, the precipitants are benzylamine and piperidine.

Quinoline will separate thorium from neodymium and zirconium from the latter, while aniline separates thorium and also zirconium from lanthanum. The latter and thorium are also separated by quinoline. With *o*-toluidine cerium may be separated from praseodymium, and the latter and thorium may be separated by aniline. Finally, xylidine will separate zirconium from lanthanum, as well as from praseodymium.

UNIVERSITY OF PENNSYLVANIA.

A NEW METHOD FOR THE APPROXIMATE DETERMINATION OF URIC ACID IN URINE.

BY JULIUS RUDISCH AND LEOPOLD BOROSCHEK.

Received March 13, 1902.

SEVERAL of the most important methods for the quantitative determination of uric acid in urine, depend on the practically complete precipitation of the uric acid, as a magnesia silver urate, by the addition of an ammoniacal silver solution and a magnesia solution to the urine.

This method of precipitation is open to several objections:

First, the ammoniacal magnesia solution causes a voluminous precipitate of triple phosphate to separate from the urine. This precipitate, if not previously removed, contaminates the silver urate precipitate, rendering filtration and washing difficult owing to its large bulk. In Ludwig's method[1] the phosphates are thrown down together with the uric acid. Salkowski[2] recommends the removal of the phosphates by means of an ammoniacal magnesia solution and filtering the urine, previous to the addition of the ammoniacal silver solution. Folin and Shaffer found[3] that if this

[1] *Ztschr. anal. Chem.*, **21**, 148 (1882).
[2] *Ztschr. physiol. Chem.*, **14**, 50 (1890).
[3] *Ibid.*, **32**, 553 (1901).

method be followed, a loss of about 0.002 gram of uric acid for 100 cc. of urine results.

Second, the ammoniacal silver solution not only precipitates the uric acid but also the xanthine bases contained in the urine.

Third, the silver precipitate obtained by this method from urine, is not entirely insoluble in dilute solutions of ammonia.

Fourth, the precipitate is generally dark colored, or gradually blackens owing to a reduction of the ammonia silver solution. Salkowski[1] also noticed this. Haycraft[2] and Herman[3] found that the addition of sodium bicarbonate hinders but does not entirely prevent this reduction.

In an attempt to do away with the use of ammonia to which at least three of the above-mentioned difficulties could be traced, a sulphite-silver solution was tried.

The solubility of silver chloride in an aqueous solution of sodium sulphite is not generally known, as no mention of it can be found in Comey's "Dictionary of Chemical Solubilities."

It was found by us that at ordinary room temperature, 100 cc. of a saturated aqueous solution of sodium sulphite dissolves about 1 gram of silver chloride. In the experimental work a twentieth normal solution, containing 7.175 grams of silver chloride in 1 liter was employed.

By adding the sulphite-silver solution, to a solution of uric acid, strongly alkaline with sodium carbonate, it was found that all the uric acid was thrown down as an almost white, flocculent precipitate which settles after several minutes and which can be readily filtered out and washed. This precipitate dissolves to a considerable extent in cold water, but is practically insoluble in dilute solutions of sodium carbonate.

From the analyses of the precipitate, the ratio of silver to nitrogen was found to agree with that calculated for 1 atom of silver to 1 molecule of uric acid. From the fact that the uric acid is completely precipitated in the absence of magnesia salts, and also that uric acid cannot form neutral salts with alkalies in the presence of carbon dioxide or soluble carbonates as claimed by Allen and

[1] *Ztschr. physiol. Chem.*, **14**, 40 (1890).
[2] *Ztschr. anal. Chem.*, **25**, 169 (1886).
[3] *Ztschr. physiol. Chem.*, **12**, 497.

Beusch[1], further, from the conditions under which the precipitation was made, it is probable that the precipitate has the following composition: $AgC_5H_3N_4O_3$.

When the sulphite-silver solution is added to urine, made strongly alkaline with sodium carbonate, a yellowish white flocculent precipitate forms, which settles after a few minutes and can be readily filtered out and washed. The precipitate does not darken during washing, or on exposure to the air. By this method the voluminous precipitate of the triple phosphates is avoided, as the addition of a considerable excess of a saturated sodium carbonate solution, to the urine, throws down only a slight precipitate. This need not be removed previous to the addition of the sulphite-silver solution. By adding from 10 to 15 grams of Rochelle salt to 100 cc. of urine it will remain clear even after the addition of an excess of a sodium carbonate solution.

A series of parallel determinations upon a number of urines were made, using both the silver-ammonia and the sulphite-silver methods of precipitation. The silver or nitrogen or both of these constituents of the precipitates were determined. By calculating all the results to uric acid, it was found that those obtained by the silver-ammonia method were from 0.001 to 0.006 gram (uric acid) higher for 100 cc. of urine, than the results obtained by the sulphite silver method.

On examining the precipitates obtained by both methods, according to the Salkowski[2] method for the determination of xanthines, it was found, that the difference in the results obtained by the two methods could be partly, if not entirely accounted for, by the fact that the sulphite-silver solution does not precipitate the xanthine bases as completely as the ammonia-silver solution. Which of the 10 xanthine bases that have been discovered in urine are, and which are not, precipitated by the sulphite-silver solution has not as yet been determined.

EXPERIMENTAL PART.

A. Uric Acid.

1. 0.150 gram uric acid was dissolved in a hot solution of sodium

[1] *Ann. Chem. Pharm.*, **65**, 181 (1848).
[2] Pflüger's *Archiv.*, **69**, 280 (1898).

carbonate and diluted to 300 cc. with water. An excess of a magnesium nitrate solution and 30 cc. of twentieth-normal sulphite-silver solution were added. After standing one-half hour, the precipitate was filtered off and washed free of the excess of silver and of chlorine with water. The precipitate and filter were digested in a Kjeldahl flask with concentrated sulphuric acid and potassium sulphate, and heated until almost colorless. On cooling, the mixture was diluted with water, the silver was separated as silver sulphide, by means of a sodium sulphide solution, and after being filtered out and washed was determined by the Volhard method. The filtrate was made alkaline with sodium hydroxide and the ammonia was distilled into a standard sulphuric acid solution.

The silver required 7 cc. of tenth-normal ammonium thiocyanate.

$$7 \times 0.0168 = 0.1176 \text{ gram uric acid.}$$

The ammonia neutralized 28 cc. of tenth-normal sulphuric acid.

$$28 \times 0.0014 \times 3 = 0.1176 \text{ gram uric acid.}$$

The ratio of the silver to nitrogen corresponds to 1 atom of silver to the molecule of uric acid. It was afterwards found that the loss of uric acid was due to the solubility of the precipitate in water.

2. 0.250 gram of uric acid was dissolved in a dilute potassium hydroxide solution (free from chlorine) and made up to 500 cc. with water.

100 cc. of this solution was titrated according to Hopkins' method. Required 13.1 cc. of twentieth-normal potassium permanganate.

$$13.1 \times 3.75 = 0.0491 \text{ gram uric acid.}$$

To 250 cc. of this solution, an excess of magnesium nitrate solution was added, 25 cc. of a saturated aqueous sodium carbonate solution, and 25 cc. of twentieth-normal sulphite-silver solution. The precipitate was filtered off and washed with a dilute solution of sodium carbonate. To the first wash solution a little sodium sulphite was also added. The precipitate and filter were placed in a beaker and boiled with concentrated nitric acid (free of chlorine). Then it was diluted with water and boiled to expel the

oxides of nitrogen. When cold the solution was titrated with a thiocyanate solution, using ferric alum as an indicator.

Required 36.6 cc. fiftieth-normal ammonium thiocyanate.

$\frac{36.6 \times 2 \times 0.00168}{2.5} = 0.0492$ gram uric acid for 100 cc. of the solution.

3. A solution of 0.250 gram of uric acid in 500 cc. was made as in (2).

I. 100 cc. by Hopkins' method required 13.3 cc. twentieth-normal potassium permanganate.

II. 100 cc. by Hopkins' method required 13.3 cc. twentieth-normal potassium permanganate.

$13.3 \times 3.75 = 0.0499$ gram uric acid in 100 cc of the solution.

To 100 cc. of the solution, 15 cc. of a saturated solution of sodium carbonate, and 10 cc. of twentieth-normal sulphite-silver solution were added. The precipitate was treated as in (2). Required 14.7 cc. of fiftieth-normal ammonium thiocyanate = 0.0494 gram uric acid.

Another 100 cc. was treated in exactly the same way. Required 14.8 cc. of fiftieth-normal ammonium thiocyanate = 0.0497 gram uric acid.

Therefore the uric acid was completely precipitated by the sulphite-silver solution in the absence of magnesium salts.

B. Experiments with Urine.

The following methods of precipitation were employed:

1. *The Sulphite-Silver Method.*—A measured amount of urine was taken. After neutralizing with a saturated aqueous solution of sodium carbonate, 15 cc. excess for each 100 cc. of urine was added, and then 10 cc. of twentieth-normal sulphite-silver solution was added. In many of the determinations an excess of magnesium nitrate solution was also introduced, but this was found to be unnecessary. After standing one hour, the precipitate was filtered off and washed free of the excess of silver and of chlorine with a dilute solution of sodium carbonate.

2. *The Ammonia-Silver Method.*—A measured amount of urine was taken. For each 100 cc. was added 10 cc. of the Ludwig mag-

nesia mixture. The urine was then diluted to a known bulk and filtered through a dry filter. An aliquot portion of the filtrate was taken and for each 100 cc. urine represented by the filtrate 5 cc. of a tenth-normal ammoniacal silver solution was added. After standing one hour, the precipitate was filtered off and washed free of the excess of silver and of chlorine with a very dilute ammonia solution. If the nitrogen of the precipitate was to be determined, it was washed with water to remove the ammonia.

To determine the silver and nitrogen contained in these precipitates the filter and precipitate were boiled with water containing a little magnesium oxide to remove the last traces of ammonia, and then the method as described under *A* 1 was followed. When only the silver contained in these precipitates was to be determined, the method described under *A* 2 was used. The results are given in the following table:

Urine.	Method of precipitation.	Silver per 100 cc. of urine.	Silver calculated to uric acid.	Nitrogen per 100 cc. of urine.	Nitrogen calculated to uric acid.
1	[1] Sulphite-silver	0.0404	0.063	...	...
	Ammonia-silver ...	0.0414	0.0645	...	...
2	[1] Sulphite-silver	0.0329	0.0507	...	...
	Ammonia-silver ...	0.0331	0.0517	...	...
3	[1] Sulphite-silver	0.0348	0.0542	0.0154	0.0462
	Sulphite-silver	0.0359	0.0558	...	...
	Ammonia-silver ...	0.035	0.0546	0.0164	0.0492
4	[1] Sulphite-silver	0.0301	0.0468	...	...
	Sulphite-silver	0.0301	0.0468	...	...
	Ammonia-silver ...	0.0339	0.0528	0.0167	0.0501
5	[1] Sulphite-silver	0.0324	0.0504	...	...
	Sulphite-silver	0.0324	0.0504	...	...
	Ammonia-silver ...	0.0339	0.0528	...	...
6	[2] Sulphite-silver	0.0274	0.0426	...	...
	Ammonia-silver ...	0.0291	0.0454	...	...
7	[2] Sulphite-silver	0.0346	0.0541	...	...
	Ammonia-silver ...	0.0363	0.0561	...	...
8	[2] Sulphite-silver	0.0229	0.036	0.0115	0.0346
	Ammonia-silver ...	0.0286	0.044	0.0141	0.0423

From the invariably lower results obtained by the sulphite-silver method, it was suspected that the xanthine bases of the urine were

[1] Magnesium solution also added.
[2] Mixed urine containing sugar.

not precipitated by the sulphite-silver solution. In order to determine this fact the following experiments were tried:

1. By means of the Salkowski method[1] the xanthine bases from 900 cc. of urine were obtained in a dilute sulphuric acid solution. This solution was diluted with water to 100 cc.

Fifty cc. of this solution were made alkaline with ammonia and the xanthine bases precipitated as silver salts by the addition of an ammoniacal silver solution. The silver contained in the precipitate was determined by the Volhard method. Required 18.4 cc. of fiftieth-normal ammonium thiocyanate.

To 50 cc. of the same solution an excess of sodium carbonate was added and then the sulphite-silver solution. The silver, in the xanthine-silver precipitate, was titrated by the Volhard method. Required 15.7 cc. of fiftieth-normal ammonium thiocyanate.

The difference in the silver content of the xanthine precipitates obtained by the two methods was therefore:

18.4 — 15.7 = 2.7 cc. fiftieth-normal ammonium thiocyanate = 0.0058 gram silver for 450 cc., or 0.0013 gram silver for 100 cc. of urine.

Calculated to uric acid this difference amounts to 0.002 gram per 100 cc. of urine.

2. The silver, in the precipitate from 100 cc. of a urine obtained by the sulphite-silver method, required 16.1 cc. fiftieth-normal ammonium thiocyanate.

The xanthine-silver, obtained by applying the Salkowski method to the precipitate from 300 cc. of urine thrown down by the sulphite-silver method, required 5.7 cc. of fiftieth-normal ammonium thiocyanate.

The uric acid in 100 cc. of this urine was

$$\left(16.1 - \frac{5.7}{3}\right) \times 2 \times 0.00168 = 0.0477 \text{ gram.}$$

Similarly the silver in the precipitate from 100 cc. of urine obtained by the ammonia-silver method, required 16.8 cc. of fiftieth-normal thiocyanate; and the xanthine-silver from 300 cc. of this urine obtained by the Salkowski method required 7.8 cc. of fiftieth-normal ammonium thiocyanate.

[1] Neubaum Vogel's "Analyse des Harns," p. 829, 10th ed.

The uric acid in 100 cc. of the urine was

$$\left(16.8 - \frac{7.8}{3}\right) \times 2 \times 0.00168 = 0.0477 \text{ gram.}$$

3. Another urine was treated in the same way.

The silver in the precipitate obtained according to the sulphite-silver method from 100 cc. of urine, required 14.8 cc of fiftieth-normal ammonium thiocyanate.

The xanthine silver, from 300 cc. of urine by sulphite-silver method, required 7.8 cc. of fiftieth-normal ammonium thiocyanate.

The uric acid in 100 cc. of the urine is

$$\left((14.8 - \frac{7.8}{3}\right) \times 2 \times 0.00168 = 0.041 \text{ gram.}$$

The silver from 100 cc. of the urine by the silver-ammonia method, required 15.5 cc. of fiftieth-normal ammonium thiocyanate.

The xanthine silver obtained by the Salkowski method from 300 cc. of the urine, required 9 cc. of fiftieth-normal ammonium thiocyanate.

The uric acid in 100 cc. of the urine is

$$\left(15.5 - \frac{9}{3}\right) \times 2 \times 0.00168 = 0.042 \text{ gram.}$$

The difference in the results found by the two methods, can be partly accounted for by the fact that the sulphite-silver solution does not precipitate the xanthine bases completely.

The use of a sulphite-silver solution instead of an ammoniacal silver solution for the precipitation of uric acid in urine, has the advantage that by its use the precipitation of the bulky earthy phosphates is avoided, the precipitate does not darken, as no reduction of the silver solution takes place and finally the precipitate can be readily filtered off and washed. The work will be continued.

LEAD THIOCYANATE.

By R. D. Hall.

Received March 21, 1902.

Normal lead thiocyanate is described by Liebig[1] as a yellow precipitate formed by the action of potassium thiocyanate on lead acetate. The salt, on standing for some time undisturbed, separates as large glistening crystals which are almost insoluble in cold water, but are decomposed by boiling with the formation of a yellow, completely insoluble basic salt. Liebig assigned the formula $Pb(CNS)_2$ to the normal salt which formula was established by analysis. The analysis of the basic salt obtained by him is in better agreement with the formula $PbO.Pb(CNS)_2$ than with $Pb(OH)(CNS)$, the formula given in the literature.

In the preparation of lead thiocyanate from pure lead nitrate and potassium thiocyanate, a compound was obtained which differed somewhat from the salt described by Liebig. The crystals were monoclinic like Liebig's but were white and appeared either in large transparent crystals or separated as a feathery mass. Analysis showed these crystals to contain 63.98 per cent. of lead while the formula $Pb(CNS)_2$ requires 64.09 per cent. They are completely soluble in hot water and crystallize from solution without suffering decomposition. 3.3 parts of lead thiocyanate dissolve in 100 parts of boiling water, while at 23° C. 0.69 of a part dissolves. Analysis of the recrystallized salt showed 64.03 per cent. of lead.

The crystals were boiled with water for several hours and showed no such decomposition as is described by Liebig, who mentions that under these conditions an insoluble basic salt is formed while at the same time the solution becomes acid. The basic salt can be obtained by the addition of potassium thiocyanate to a solution of basic lead acetate and appears as a white precipitate. The salt prepared in this way shows a lead content of 73.3 per cent. of lead. That required for $Pb(OH)(CNS)$ is 73.2 per cent., while the salt obtained by Liebig by the addition of ammonia to a mixture of normal lead acetate and potassium thiocyanate or

[1] Pogg. *Ann.*, **25**, 546.

by the decomposition of the normal lead thiocyanate by boiling water, contained 74.96 per cent. of lead, corresponding more nearly to the compound $PbO.Pb(CNS)_2$ which requires 75.7 per cent. of lead. Basic lead thiocyanate is sparingly soluble in boiling water, and crystallizes from hot solutions in small acicular crystals. It is less soluble in water than chloride and more soluble than chromate of lead.

In seeking to ascertain the cause of the yellow discoloration of lead thiocyanate as obtained by Liebig, an investigation was made of the effect of the presence of other salts on the character of the precipitate. It was found that, if the lead solution contains iron, mercury or bismuth salts, the product formed by the addition of potassium thiocyanate is yellow. If a considerable amount of iron is in the solution from which lead thiocyanate is precipitated, the precipitate is yellow with a decided pink cast, while the liquid shows the intense red coloration of ferric thiocyanate. The substance thus obtained, when washed and boiled with water, leaves a residue which resembles ferric hydroxide. When mercuric salts are present in the solution from which lead thiocyanate is obtained, the latter is greenish yellow and is completely soluble in hot water.

The effect of bismuth in the solution has been carefully studied. Basic bismuth thiocyanate was prepared by treating a solution of bismuth oxide in acetic acid with potassium thiocyanate. The white basic salt separates out on heating, while the mother-liquor, when concentrated, yields the finely divided red normal salt. When lead acetate solution contains a small quantity of bismuth acetate, the precipitate which appears by the addition of potassium thiocyanate, comes down slowly and is yellow and crystalline. Analysis of the yellow salt showed 63.8 and 63.95 per cent. of lead, while the normal salt contains 64.09 per cent. While the per cent. of lead is only slightly less than that of the theoretical, the crystals were distinctly yellow, due to the bismuth which they contained. A distinct reaction for bismuth was obtained, after removing the lead as sulphate, by the addition of an alkaline solution of stannous chloride. Moreover all but a very small quantity of the salt dissolved in boiling water. When the solution was filtered, the clear liquid showed an acid reaction and on cooling white crystals appeared. The residue gave a decided reaction for bismuth and

none whatever for lead, showing the bismuth salt to be contained in the lead thiocyanate crystals as impurities which can be removed by crystallization.

Normal solutions of lead nitrate and bismuth nitrate, mixed in various proportions, were precipitated with potassium thiocyanate. The precipitate in each case was filtered, washed rapidly with water, then with alcohol, and dried in an air-bath. The substances thus obtained varied in color from a light yellow to a dark red, depending on the ratio of bismuth to lead in the original solution; the more bismuth the darker was the resulting salt. As nitric acid readily oxidizes lead thiocyanate to sulphate, it is necessary to immediately remove the salt from the liquor by filtration. The precipitates contained varying amounts of bismuth from a trace up to from 6 to 7 per cent. No relation could be determined between the amount of lead thiocyanate and bismuth thiocyanate in the precipitate pointing to the formation of a definite double salt, neither was there any noticeable relation between the amounts of bismuth and lead in the solution to that of bismuth thiocyanate and lead thiocyanate in the precipitate, except the general one that the more bismuth in the solution the more in the precipitate.

A solution which contained 10 cc. of normal bismuth nitrate and 100 cc. of normal lead nitrate gave, with potassium thiocyanate, a precipitate that contained 61.7 per cent. of lead and 2.05 per cent. of bismuth, which is about the proportion of 1 part of bismuth to 30 parts of lead, while the ratio in the solution was 1 part of bismuth to 10 of lead. Where the ratio in the solution was 1 of bismuth to 2 of lead, the salt obtained by the addition of potassium thiocyanate contained 2.8 per cent. of bismuth and 60.8 per cent. of lead, or in about the proportion of 1 part of bismuth to 22 parts of lead. The precipitate from a solution containing five times as much bismuth as lead contained nine times as much lead as bismuth, analysis showing 56.4 per cent. of lead and 6.3 per cent. of bismuth.

Cold water slowly decomposes the yellow salt thus formed, washing away the lead salt and leaving the bismuth. On boiling, all of the lead salt goes into solution leaving a nearly white gelatinous residue, while the liquid becomes acid. Extraction with water does not give a complete separation, as some bismuth is ex-

tracted along with lead. Repeated crystallization will entirely remove the yellow color of the lead thiocyanate. It requires only a trace of bismuth in the solution to give a decided yellow cast to the precipitate, yet a considerable quantity is necessary before enough bismuth is present to appear as a residue when dissolved in boiling water.

Lead thiocyanate is white when pure but is readily contaminated by the presence of foreign salts, especially bismuth, in the solution from which it is precipitated. It is entirely soluble in hot water crystallizing out unchanged on cooling, and can be purified by repeated crystallization. Basic lead thiocyanate can not be prepared by boiling the normal salt with water, but must be prepared from a solution of a basic salt such as the acetate.

UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 63.]

AMMONIUM VANADICOPHOSPHOTUNGSTATE.

BY EDGAR F. SMITH AND FRANZ F. EXNER.

Received March 26, 1902.

During the summer months of 1901 large quantities of wolframite were examined by us for the purpose of ascertaining just what minute constituents were present in it, which might possibly contaminate the tungstic acid derived from this source. That such impurities existed in tungstic acid seemed very probable as the numerous attempts to fix the atomic weight of tungsten, by reduction of the oxide in hydrogen and subsequent oxidation of the tungsten metal, gave unsatisfactory results. The difference between the maximum and minimum values seemed too great to be attributed entirely to the inefficiency of the method so it was determined to seek for impurities, some hint as to the nature of which it was thought could be best realized by taking into study large quantities of the starting-material—wolframite, from Lawrence County, South Dakota.

The finely divided material was decomposed by prolonged digestion with aqua regia. The hydrated tungstic acid, after filtration and thorough washing, was digested with ammonia water.

This solution gave on evaporation large yields of ammonium paratungstate, which after two or three recrystallizations was perfectly white in color. Portions of the same were ignited to trioxide and the latter digested with a 2 per cent. sodium carbonate solution, after the manner of Taylor,[1] when the white residue observed by him remained. It showed the presence of iron, manganese and tungstic acid. Portions of the same ammonium paratungstate were recrystallized ten times from water, the first portions only being used. The tungsten trioxide from the tenth crystallization, when digested with sodium carbonate, left a white residue in which iron, manganese and tungsten were found as before. This proves that mere crystallization, although repeated many times, fails to eliminate this peculiar compound, noticed by Taylor, which most probably has contaminated all tungstic acid derived from wolframite. It could easily occasion the peculiar rise and fall observed in the many atomic weight determinations made during the last fifty years. We shall, however, refrain from further comment on this point, as the purification of tungstic acid is still under investigation in this laboratory.

Those persons who have made ammonium paratungstate from wolframite have surely noticed the dark color of the mother liquor from the salt. In our work the concentration of the mother liquors was continued until their color was black. The ammonium paratungstate was placed to one side, the mother liquors alone being watched. They became very heavy with increased concentration until finally, after great reduction in volume, greenish yellow masses separated, in which brownish octahedral crystals were found. In the filtrate from the greenish masses additional octahedral forms, now perfectly black in color, separated. The greenish material was removed with difficulty from these crystals. But eventually we discovered that if the dark-colored solutions of the octahedral forms were boiled with pure precipitated calcium carbonate the contaminations of the octahedral substance were entirely eliminated and that the concentrated liquids now yielded brilliant black and quite large octahedra. A half pound of these forms was obtained from the wolframite from Dakota and also from impure ammonium paratungstate made from Connecticut

[1] Thesis for Ph.D., 1901.

wolframite. This compound puzzled us. It showed the presence of ammonia, water and tungstic acid, with a small amount of iron and manganese. That it contained ammonia and tungstic acid and did not give these up when boiled with calcium carbonate, suggested the advisability of boiling aqueous solutions of ammonium paratungstate and ammonium metatungstate with calcium carbonate. The tungstic acid in each case was quantitatively precipitated (or nearly so). Ammonium molybdate also surrendered its molybdic acid content completely to the same reagent.

The question then arose why does not the black, octahedral substance yield its tungstic acid content under similar treatment? Ammonium paratungstate and ammonium metatungstate, when heated with acids, yield tungstic acid. The octahedral compound was boiled for six hours with concentrated hydrochloric acid and three hours more with aqua regia, but tungstic acid did not separate. Evidently the tungstic acid in it was held in a peculiarly combined condition. Boiling with ammonia water caused no change. Fusion with sodium carbonate decomposed the compound. The cold fusion showed a slight bluish tinge, indicating manganese, and on dissolving it in water a slight amount of iron and manganese oxides remained (about 1.20 per cent.). The alkaline aqueous solution, when warmed with hydrochloric acid, gave a precipitate of tungstic acid, which soon acquired a deep orange color. When the black crystals were decomposed with acid potassium sulphate, the cold fusion showed a rosin-like appearance. It dissolved partly in water. The aqueous solution was reddish yellow in color, while the residue was white. The solution, acid in reaction, when acted upon by hydrogen sulphide became amethystine in color; the same coloration was noticed when portions of the solution were saturated with sulphur dioxide. The mystery increased.

A reaction frequently used in this laboratory in the past in the purification of tungstic acid, to expel molybdic acid, was now tried; *viz*: the black crystals were ignited in a crucible, and after reduction to powder, were exposed in a porcelain boat to dry hydrochloric acid gas, when to our amazement a brown-colored liquid appeared in the anterior portion of the tube. On drying, this became greenish blue in color. The acid water in the receiver

showed a faint blue tinge which upon concentration of the solution became more intense, indicating *the presence of vanadium,* which was definitely established by the hydrogen peroxide test as well as by other reactions. Thus, vanadium, a hitherto unsuspected impurity in tungstic acid, was found. But, it might fairly be asked, is it probable that this element exists in ammonium paratungstate? A portion of the latter, perfectly white in color after four recrystallizations from water, was examined and it disclosed vanadium!

Returning to the black salt it may well be asked why did the sulphuric acid solutions mentioned above take on an amethystine color when they were exposed to the action of hydrogen sulphide and of sulphur dioxide? Surely the presence of small amounts of tungstic acid could not cause this behavior, for ammonium vanado-tungstate, prepared according to the recommendation of Dr. Wolcott Gibbs, showed a red or reddish yellow colored solution and gave the blue color characteristic of vanadium when reduced with hydrogen sulphide or sulphur dioxide, after the removal of the major portion of the tungstic acid. How was the peculiar color of the vanadium solution we were studying to be explained? Upon adding ammonium phosphate to ammonium vanadate containing ammonium tungstate, all in aqueous solution, then acidulating with sulphuric acid and reducing the liquid with hydrogen sulphide or sulphur dioxide, an amethystine red color will be produced and not a trace of the blue, always given by vanadium. So at last the abnormal behavior of the latter in the presence of well known reducing agents could be explained. It was due to the presence of phosphoric acid. When some of the black crystals were dissolved in water, and nitric acid and ammonium molybdate added to this solution, the familiar yellow ammonium phosphomolybdate revealed itself.

The puzzle was now solved. The black octahedral salt contained ammonia, water, tungsten, vanadium and phosphorus, with traces of iron and manganese. It was concluded that we had in hand an ammonium phospho-vanado-tungstate. The literature on "complex inorganic acids" gave us no information upon derivatives of this constitution. Assuming that the salt was of this class we employed for its analysis the method of Wolcott Gibbs and also

a method by the same chemist, modified by Friedheim, for vanado-tungstates, but to our surprise both failed, because of the presence of phosphoric acid, so that it was necessary to devise a new method which will be described later elsewhere. It will suffice for the present to mention that success in the analysis was finally reached, and the results are accordingly given as follows:

	Per cent.	Per cent.
$(NH_4)_2O$	5.40	5.27
H_2O	11.85	12.25
WO_3	75.94	75.71
P_2O_5	0.99	0.94
V_2O_3	4.03	4.01
Fe_2O_3	1.19	1.07
MnO	0.04	0.05
	99.44	99.30

Ammonium phospho-vanadates and vanado-tungstates are yellowish red to red in color in aqueous solution. On boiling ammonium tungstate, vanadate and phosphate together, deep red colored solutions resulted. Consequently we were at a loss to account for the brownish black to black color of the aqueous solution of our new salt until after considerable experimenting it was discovered that by the use of vanadium trioxide (V_2O_3) with ammonium phosphate and ammonium tungstate black colored solutions were obtained, from which octahedral forms crystallized, containing ammonia, water, tungstic acid, vanadium trioxide and phosphorus pentoxide. Regarding the iron and manganese as adventitious substances and deducting them the percentages of the remaining constituents were about identical with those obtained from a salt which was later prepared as indicated immediately above. The new compound, isolated from the mother-liquors of ammonium paratungstate, is a representative of a new group of derivatives. It may be termed ammonium vanadicophosphotungstate,

$$(NH_4)_2O.V_2O_3.P_2O_5.WO_3.XH_2O.$$

It suggested the possibility of forming vanadophosphotungstates, vanadoarsenotungstates, vanadicovanadotungstates, etc., etc. Thirteen such complex bodies have been made and remade. Their analyses are most satisfactory. They will be described later by Mr. Allen Rogers, who is now occupied with their investigation.

It is needless to add that molybdic acid may be substituted for tungstic acid in all these bodies, and very likely columbic and tantalic oxides may be introduced for vanadic, arsenic and phosphoric oxides, and also with them, thus opening up a new and extensive class or group of acids which we hope to study as time permits.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 62.]

A NEW QUALITATIVE TEST FOR COBALT.

BY J. L. DANZIGER.

Received March 17, 1902.

THE following test, if carried out properly, will serve to detect the presence of cobalt, in a solution containing 1 part of cobalt, in 500,000 parts of water, provided the solution is colorless or but slightly colored, which can readily be obtained by dilution.

To about 5 cc. of the solution, acid with hydrochloric acid, in a test-tube, there is added solid ammonium thioacetate, CH_3COSNH_4, a few drops of stannous chloride solution, and an equal volume of amyl alcohol, or a mixture of acetone and ether or of alcohol and ether; the whole is well shaken and allowed to separate. If any cobalt is present, the upper layer will be colored blue, the intensity of the color depending on the amount of cobalt present. Solid ammonium thioacetate is added to prevent dilution of the solution, since water destroys the blue color. Stannous chloride is added to reduce any iron present, since ferric iron gives a deep red coloration, as with ammonium thiocyanate. Amyl alcohol, a mixture of acetone and ether or of alcohol and ether, is added to diminish the dissociation and extract the color produced by the undissociated cobalt salt. Amyl alcohol was found to be the most efficient, but is objectionable on account of its disagreeable odor.

In order to ascertain to what compound the color was due, a large amount was prepared by the addition of a saturated solution of ammonium thioacetate to a saturated solution of cobalt chloride, the solution extracted with a mixture of acetone and ether, and the ethereal solution evaporated.

After trying a great number of solvents, it was found impossible to crystallize the substance; so it was washed free from impurities, and its formula deduced from the ratio of cobalt, ammonium, and sulphur present as follows:

About 1 gram of the substance was dissolved in water, an excess of potassium hydroxide added, and the ammonia distilled into a known excess of standard acid, the excess of acid being determined by standard alkali.

The residue in the flask, consisting of cobalt sulphide, potassium sulphide, etc., formed by the decomposing action of the hot strong alkali, was diluted and filtered. The precipitate was treated with a large excess of fuming nitric acid, to oxidize the sulphur, the excess of nitric acid boiled out and the cobalt twice precipitated with potassium hydroxide, dissolved in nitric acid and precipitated as cobalt ammonium phosphate, as described by Dakin[1], except that alcohol was added to render the precipitation complete, and finally weighed as cobalt pyrophosphate, $Co_2P_2O_7$.

The first filtrate from the cobalt, containing sulphides, was oxidized with fuming nitric acid, combined with the other filtrates and the sulphur precipitated as barium sulphate, ignited and weighed.

The analysis was run in duplicate, the results being:

			Molecular ratios.		
	Gram.	Gram.	I.	II.	Average.
NH_4.....	0.06625	0.07965	1.96	2.03	1.99
S.....	0.23650	0.27970	3.95	4.01	3.98
Co.....	0.11000	0.12866	1.00	1.00	1.00

These ratios approximate 2:4:1, and correspond to the formula $(CH_3COS)_2Co.2CH_3COSNH_4$.

A number of tests were made to compare the sensitiveness of the test with the thiocyanate test proposed by Vogel[2] and described by Treadwell.[3]

Several solutions of cobalt chloride were prepared, of dilutions varying from 1:5,000 to 1:50,000. To equal amounts of each of these solutions, quantities of ammonium thiocyanate and of ammonium thioacetate, sufficient to saturate them, were added, and

[1] *Chem. News*, Jan. 25, 1901, p. 37.
[2] *Ber. d. chem. Ges.*, **12**, 2314 (1879).
[3] *Ztschr. anorg. Chem.*, Jan., 1901, p. 108.

then an equal volume of amyl alcohol. The colors of the upper layers were then compared, and were found to be of equal intensity for each dilution. The thiocyanate test was found to be much more sensitive than Treadwell claimed.

Attention is called to the fact that the double ammonium cobalt thioacetate has 2 molecules of ammonium thioacetate to 1 of cobalt thioacetate; this is analogous to the double ammonium cobalt thiocyanate.

QUANTITATIVE LABORATORY,
March 11, 1902.

A NOTE ON THE VOLUMETRIC DETERMINATION OF COPPER.

BY S. W. PARR.

Received March 31, 1902.

THE volumetric method for copper recently described,[1] wherein the cuprous thiocyanate is titrated directly with permanganate, first in the alkaline and then in the acid condition, is found at times to give an unsatisfactory end reaction. This seems to be due to an incomplete oxidation of the cuprous hydroxide by the permanganate, the latter acting somewhat slowly under the conditions described. Upon acidifying, therefore, any copper remaining in the cuprous condition reverts to the cuprous thiocyanate and in this form is slowly acted upon by the permanganate; hence the occasional indefiniteness at the end.

This difficulty is very easily overcome by the following slight modification: The washed precipitate of cuprous thiocyanate and the asbestos pulp having been returned to the beaker, there is added 10 cc. of a 10 per cent. solution of potassium hydroxide, followed by 10 cc. of ammonia (sp. gr. 0.96) then, without delay, the titration is begun with the standard permanganate solution, continuing until, upon warming, the green color of the supernatant liquid remains. The heating should not be prolonged, 45° to 55° being quite sufficient. Add now a sight excess of permanganate equal to one-third or one-fourth of the quantity needed to produce the permanent green coloration. Allow the mixture to stand for five

[1] This Journal, **22**, 685.

minutes, acidify with about 25 cc. of a mixture of concentrated sulphuric acid and water (1 of acid to 1 or 2 of water, cooled to a moderate temperature), and complete the titration to the usual pink coloration. Some heat is developed upon adding the acid to the alkaline solution, but this is without harmful effect. The end reaction is sharp and the results are concordant. The copper in a solution of copper foil was determined electrolytically and also by the above modification with results as follows:

	Electrolytically.	Burette readings.
(*a*)	0.0442	29.3
(*b*)	0.0443	29.3
(*c*)	0.0442	29.3
(*d*)	0.0443	29.25
(*e*)	...	29.2
(*f*)	...	29.3
(*g*)	...	29.3

The iron value of the permanganate multiplied by 0.1602, and the resulting copper factor multiplied by the burette reading 29.3, gives 0.04430 gram of copper as against 0.04425 of electrolytic copper.

To show the concordant nature of the results obtained by this procedure, the readings from the titrations on four ores of widely different character are given as follows:

A.	B.	C.	D.
23.7	10.8	16.2	12.3
23.7	10.8	16.2	12.2

In case of bearing metals, etc., containing both lead and tin, one or the other must be removed because of the formation presumably of lead stannite, which reduces permanganate.

UNIVERSITY OF ILLINOIS.

THE AMERICAN ELECTROCHEMICAL SOCIETY.

BY JOSEPH W. RICHARDS.

PURSUANT to a call for a meeting signed by C. J. Reed, Carl Hering, E. F. Roeber, W. H. Wahl, of Philadelphia, and J. W. Richards, of Lehigh University, a preliminary meeting to found the above-named society was held at the Engineers' Club, Philadelphia, on November 1, 1901. As the result of that meeting, the

first general meeting of the proposed society was called for April 3d, 4th, and 5th, in Philadelphia, and committees were appointed to enroll members and secure papers.

The meeting for organization was called to order at 8 P.M., April 3rd, in the assembly hall of the Manufacturers' Club, in Philadelphia, with Dr. J. W. Richards in the chair and Carl Hering, secretary *pro tem.* Reports of committees showed that 357 persons had announced themselves for membership, and that 28 papers had been offered for reading at the meeting. The society then organized with title as above, and elected as officers the following:

President.—Prof. Joseph W. Richards, Ph.D., Department of Metallurgy, Lehigh University, and Vice-President of The American Chemical Society.

Vice-Presidents.—Prof. Charles A. Doremus, College of the City of New York; Prof. H. S. Carhart, University of Michigan; Charles M. Hall, Niagara Falls; Dr. W. D. Bancroft, Cornell University; Dr. Louis Kahlenberg, University of Wisconsin; Dr. W. R. Whitney, Massachusetts Institute of Technology.

Board of Managers.—Carl Hering, Dr. E. F. Roeber, Dr. Samuel Sadtler, of Philadelphia; E. G. Atcheson, Niagara Falls; C. O. Mailloux and W. D. Weaver, New York; Edward Weston, Waverly Park, N. J.; Dr. Samuel Sheldon, Brooklyn Institute of Technology; Colonel Samuel Reber, U. S. A., Washington, D. C.

Treasurer.—Dr. Pedro G. Salom, The Bourse, Philadelphia.

Secretary.—Charles J. Reed, 3313 N. 16th St., Philadelphia.

It was decided to hold two meetings annually and to publish separately the transactions of each meeting. The entrance fee was fixed at five dollars; annual dues five dollars. The next meeting was announced to be held at Niagara Falls the 15th to 18th of September, 1902.

On Friday, April 4th, the society met in the John Harrison Laboratory of Chemistry of the University of Pennsylvania, at 9 A.M., and at the morning session read and discussed the following papers:

A University Course in Electrochemistry, by Joseph W. Richards, Ph.D., Lehigh University.

Graphite Electrodes, by Clarence L. Collins, 2nd, Niagara Falls.

Note on the Gladstone-Tribe Couple, by Prof. W. D. Bancroft, Cornell University.

The Nascent State, by C. J. Reed, Philadelphia.

The Electrolytic Reduction of Lead, by Pedro G. Salom, Ph.D., Philadelphia.

The Refining of Composite Metals, by Titus Ulke, Sault Ste. Marie, Canada.

After lunch in Houston Hall, where the Society was the guest of the University of Pennsylvania, the meeting was resumed in the hall of the new Randal-Morgan Laboratory of Physics, and the following papers were read and discussed:

A Novel Concentration Cell, by Prof. H. S. Carhart, University of Michigan.

The Manufacture of Carbon Bisulphide in the Electric Furnace, by Edward R. Taylor, Penn Yan, N. Y.

Current Electrochemical Theories, by Prof. L. Kahlenberg, University of Wisconsin (read by Prof. C. F. Burgess).

A Zinc-Bromine Storage Battery, by Herbert H. Dow, Midland, Mich.

Continuous Electrolysis of Solutions of Metals, by N. S. Keith, Ph.D., New York City.

A Method of Electrolytic Production of Zinc from its Ores, by Samuel S. Sadtler, Philadelphia.

The Electrolytic Rectifier, by Prof. C. F. Burgess, University of Wisconsin and Carl Hambeuchen, Madison, Wis.

Caustic Alkalies and Chlorine by the Dry Electrolytic Process, by C. E. Acker, Niagara Falls.

On the Relative Speed of the Ions in Solutions of Silver Nitrate in Pyridine and Aceto-Nitrile, by Herman Schlundt, Ph.D., Madison, Wis. (read by Prof. W. D. Bancroft).

On the evening of April 4th, an informal reception was held in the parlors of the Manufacturers' Club, where the members had full opportunity of cultivating each other's personal acquaintance.

On Saturday, April 5th, the sessions were resumed in the John Harrison Laboratory of Chemistry, with reading and discussion of the following:

On a New Type of Electrolytic Meter, by Konrad Norden, Ph.D., New York City.

The Reversible Copper Oxide Plate, by W. McA. Johnson, Hartford, Conn.

A Thermodynamical Note on the Theory of the Edison Battery, by Dr. E. F. Roeber, Philadelphia.

Electrolysis of an Aqueous Solution by Alternating Current, by J. W. Richards, Ph.D., Lehigh University.

The Atom of Electro-Chemistry, by Arvid Reuterdahl, Providence, R. I.

The papers presented were all freely discussed, and the discussion, being taken down stenographically, will be published with the papers.

On the afternoon of April 3rd, a party of about thirty visited the chemical works of Harrison Bros. & Co., Inc., where various chemical processes were seen, particularly the manufacture of sodium and nitric acid by Darling's process of electrolyzing fused sodium nitrate. On the afternoon of the 5th, over thirty participated in a trip to Bethlehem, Pa., where an hour was spent in the works of the Lehigh Zinc and Iron Co., two hours in the armor-plate and heavy-forging plant of the Bethlehem Steel Co., and a short visit was made to the Lehigh University.

Altogether, nearly 100 members of the new society were in attendance; every paper presented was received attentively and discussed freely, and the membership dispersed, feeling that a move had been made which will react with great energy on the development of the youthful science and industry—that of Electro-chemistry.

NEW BOOKS.

The Letters of Jöns Jakob Berzelius and Christian Friederich Schönbein, 1836–1847. Edited by Georg W. A. Kahlbaum, Bâle. Translated by Francis V. Darbishire and N. V. Sidgwick. London: Williams and Norgate. 1900. 112 pp. 12mo. Price, three shillings.

Schönbein, the illustrious discoverer of ozone, guncotton and collodion, was a voluminous letter writer; he corresponded with Faraday and other Englishmen, with Eisenlohr of Karlsruhe, Liebig, Pettenkofer, Wöhler, and other eminent German physicists and chemists, with some Swiss, including Marig-

nac, de la Rive and Agassiz, with Henri Sainte Claire Deville and Dumas, in France, as well as with the great Swede Berzelius. Of these letters, numbering more than 1500, two groups have been published by Prof. Georg W. A. Kahlbaum and others, those exchanged with Faraday and those with J. J. Berzelius.

The first six letters of the series in the volume under review refer to the passivity of iron, independently observed, but not discovered by Schönbein, as the phenomena had been described by James Keir as early as 1790. The balance of the correspondence concerns chiefly ozone. In the long letter, dated April 14, 1844, Schönbein writes he has finally decided that the odoriferous principle produced by electrolysis of water, etc., is identical with chlorine, and he gives five reasons for believing this. The fact that ozone is a form of oxygen was suggested to Schönbein on April 20th, in the following year by Plantamour of Geneva.

The discovery of parchment paper is announced in a letter dated March 5, 1846. Three months later Schönbein refers to guncotton as a substance already known, and mentions experimenting with it in small firearms, large guns, and using it for blasting purposes in a tunnel.

This exchange of letters was terminated only by the death of Berzelius in 1848.

Chemists will find this volume an interesting contribution to the history of the science during the period embraced.

HENRY CARRINGTON BOLTON.

A TRAVERS LA MATIÈRE ET L'ENERGIE. PAR LE DR. F. E. BLAISE. Paris: Librairie Ch. Delgrave. 1902. 8vo. 344 pp. Prix, broché: 12 fr.

This volume is another example of that strong tendency which is at present manifesting itself on the part of scientific men to write on general philosophical themes. After an introduction covering six pages, the subject matter is treated in six parts, as follows: electrochemistry and mechanics, 122 pp.; matter, 20 pp.; the formation of bodies in space and their luminosity, 8 pp.; electricity, 39 pp.; electrical induction, 102 pp.; philosophical views and conclusions, 34 pp.

The author assumes the existence of a prime ether and then seeks to explain all phenomena as resulting from movements of

the particles of ether. He endeavors to show that the laws of conservation of energy and of matter, as well as all other known laws of chemistry and physics, can be deduced from the basis of his fundamental assumption. He considers atoms as made up of ether particles, and light and electricity as movements of ether. In speaking of organized beings, it is argued that since ether particles unite to form the atoms, the latter are organized and so all matter is organized. Remarks on the application of the laws of electricity and mechanics to the solution of social and moral problems, and on the absolute necessity of the existence of a form of energy capable of intelligence, imagination and volition, form an important portion of part six, which is concluded with a tirade against Darwinism and an attempt to parallel religious dogmas with scientific truths.

The book bears evidence that its author has studied a great variety of subjects; but the relations that he attempts to express are frequently vague and indefinite, and the scientific terms employed are not always correctly used. This appears, for example, in the attempt to explain the relation between Avogadro's hypothesis, Faraday's law, and the law of Dulong and Petit. The energy idea may be said to dominate the book, and yet on page 41 is the statement that according to Faraday's law chemically equivalent quantities of different substances are separated out by the same amount of energy. This clearly shows that the author does not make the very necessary distinction between energy and its factors.

The fundamental assumption that atoms are made up of ether particles is old. And while the author's endeavors to explain diverse well known laws of nature on the basis of this hypothesis are often interesting and suggestive, they are frequently based on further auxiliary assumptions, or are nothing more than mere similitudes. This is strikingly illustrated, for instance, by the comparison of tendencies for good and evil with the action of a mechanical couple and with positive and negative electrical induction. In speaking of Darwinism, surprise is expressed that the conceptions it involves should in this enlightened age have been produced, accepted and perpetuated. Species are considered as unchangeable as atoms themselves—apparently the primal assump-

tion that the latter are composite and consequently not necessarily unchangeable, is overlooked in this connection. Finally the parallelisms between religious dogmas and scientific truths, while in some respects amusing reading, are largely vague, fanciful comparisons, which can hardly be classed as stimulating intellectually or uplifting spiritually. LOUIS KAHLENBERG.

SEWAGE AND THE BACTERIAL TREATMENT OF SEWAGE. By SAMUEL RIDEAL, D.Sc. (London). Second edition. London: The Sanitary Publishing Co., Ltd. New York: John Wiley & Sons. 1901.

This book is the most comprehensive treatise that has yet appeared on the treatment of sewage. It is so good in a great many respects, that it seems almost ungracious to point out defects, yet in logical arrangement and clearness of statement it leaves much to be desired, and it seems to the reviewer, that though it contains a large amount of most valuable information, and experimental data, it does not give a very clear insight into the practical working of the various processes of sewage treatment. This may be explained by the fact that the book is evidently written from a student's point of view, and the author consequently does not take up the details of construction of plants, nor describe at all fully the practical methods of working the various processes, but rather devotes himself to explaining the changes that the sewage undergoes, and the cause or reason of these changes.

The first five chapters, about one-third of the book, are devoted to the following subjects: Chemical Analyses of Sewage and Effluents, Bacteria Occurring in Sewage, The Changes Produced by Bacteria and Enzymes. Of these chapters, that on chemical analysis is the least interesting, and certain of the methods given, especially that of determining the amount of free ammonia by adding Nessler's solution directly to the sewage, after dilution with water free from ammonia, is open to criticism. The chapters on bacteria, and the changes brought about by bacteria, and enzymes, are well written, but that the reactions as given for the decomposition of carbohydrates and fats, take place in the septic tank, is somewhat doubtful, and in fact it is questionable if any large amount of fat or grease is decomposed in a septic tank.

The remaining chapters of the book are a study of the various processes of sewage treatment: Irrigation and Sewage Farming,

Subsidence and Chemical Precipitation, Sterilization, Contact Beds, Septic Tanks, Continuous Filtration, Agricultural Value of Sewage Effluents, Distribution of Sewage upon Filters, Treatment of Trade Effluents.

These chapters are most interesting reading, being a very full compilation of the results that have been obtained during the past ten years in England. The data they contain is most valuable, but it seems as though too little attention had been paid to the order in which the results are given. Facts relating to the same process are separated from each other, and it is too often necessary to refer to the index to obtain a knowledge of all the data concerning any one process. The only process that has been rather overlooked is Intermittent Filtration, only three pages in all being devoted to the subject. This is to be regretted, as not only was "Intermittent Filtration" the first of the modern bacterial methods, but also the first to show that sewage could be purified on a practical scale by means of bacteria, and it is a method that has, in many places, given excellent results.

It is also to be wished that the author had more often given his personal opinion on the value of the experiments described, for the value of experiments depends on the character of the work, and one has very often to change the opinion formed from reading an account of a process of sewage treatment, after visiting the plant and investigating for himself the methods by which the data were obtained.

A decisive proof, however, of the value of the book taken as a whole, is the fact that it is only a little over a year since the first edition was published, and it can truly be said that it is a book which is essential to every one engaged or interested in the problem of sewage treatment. LEONARD P. KINNICUTT.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By HARRY C. JONES, Associate Professor of Physical Chemistry in the Johns Hopkins University. New York: The Macmillan Company. 1902. Price, $4.00.

The importance of physical chemistry, not only as a remarkably fruitful separate branch of science, but also as a most valuable aid in the investigation of problems in many other branches of natural science, such as chemistry proper, physics, geology, biology, physiology, medicine, is now becoming recognized so universally, that

the time may be said to be near or to have already been reached, when no student of science in any one of the above subjects can afford to neglect the study of physical chemistry in his preparation for his future profession. The demand on colleges and universities for adequate instruction in physical chemistry for many classes of students is bound to increase very rapidly. Such a book as the one written by Professor Jones will aid very much in enabling the student to take up the subject with comparatively little difficulty; it presents every side of the subject in a style notably clear and simple; it is sufficiently elementary to form an excellent introduction to physical chemistry and sufficiently thorough, both in the treatment and in its references, to show the student what books and literature he must consult in order to study any particular subject more thoroughly. In this way the book may be said to occupy a place between such other notable works on physical chemistry available for English readers, as Walker's "Introduction to Physical Chemistry," which is somewhat more elementary in character than the present work, and Nernst's "Theoretical Chemistry," and Ostwald's "Outlines of General Chemistry," which are rather more advanced. Professor Jones' book presupposes a knowledge of college physics and chemistry, inorganic and organic; elementary calculus would be necessary in order to follow very closely certain parts of the book, but it is not absolutely essential for an intelligent grasp of the general subject; for a complete mastery of the book and its subject, a knowledge of calculus would be indispensable. The work is designed for students in the later stages of their college work and the earlier part of their university career.

The brief, but carefully prepared, historical sketches introducing many of the chapters, as, for instance, the one on "Chemical Dynamics and Equilibrium," and the great number of references to original papers form excellent features of the book. The marked enthusiasm with which the author writes as a worker in the field, is bound to interest the student in the subject as a living one, with many vital problems yet to be solved. In view of this undeniable gain in stimulating the interest of the intelligent reader, the somewhat disproportionate prominence given the author's own work, considering the general character of the book, may be considered

as pardonable. It is rather surprising, for instance, in glancing over the index as a condensed illustration of this point, to find the name of our greatest American investigator in the realm even of the "new" physical chemistry, J. Willard Gibbs, entirely missing (he is named once, with honor, on page 491); and it is, perhaps, somewhat amusing to find in the same index the author's name referred to about twice as often as van't Hoff's, whereas in Nernst's "Theoretische Chemie" the proportion is as 25 to 1 in favor of the great discoverer of the relations between osmotic pressure and gas pressure. But, as stated, the stimulating effect of the breezy enthusiasm of the author may be said to offset this fault.

Where much weight is laid—justly—on the extremely important services of the theory of ionization in explaining, qualitatively and quantitatively, in a very simple and beautiful manner any number of otherwise complex phenomena in every field of chemistry, it behooves us, in order to keep the theory above reproach, to be particularly careful not to insist on the adequateness of the theory of ionization in explaining reactions, where experimental facts have been discovered and confirmed that must raise very serious doubts as to the complete correctness of such an explanation. Such a case is Ostwald's beautifully simple theory of indicators.[1]

As the book under discussion, in common with such prominent recent works on physical chemistry as those by Ostwald, Nernst, and Walker, still shows an unquestioning faith in this theory, and no reference to the other side of the problem has been seen in any other text-book, the writer would like to indicate very briefly what the other side is.

According to Ostwald, as is well known, the change of color, in the case of an indicator like phenolphthalein, is ascribed to the change simply from the colorless molecular condition,

$$\underset{\llcorner\!\!_\!\!_\!\!_

Phenolphthaleïn, as a very weak acid, would, indeed, be practically non-ionized in aqueous solution, especially in the presence of even a very small excess of hydrogen ions (from any acid); its alkali salts, undoubtedly would be highly ionized. But nevertheless the change in color is, almost certainly, not due primarily, merely to the change to the ionic condition. As early as 1892, Bernthsen[1] made it appear extremely probable that the color change is really due to a *change* of *constitution* from the colorless lactoïd, form I (with no chromophoric group), to the colored quinoid, form III (with a quinone chromophore),

$$(NaOOC.C_6H_4)(HOC_6H_4)C=C_6H_4=O. \qquad (III)$$

This salt is undoubtedly ionized in solution, but the dry molecular, silver salt is also intensely colored (violet), and the change from the colorless to the colored form of phenolphthaleïn is, therefore, primarily due to a change of constitution. This view is in far better accord with our whole knowledge of color in organic compounds than Ostwald's. The strongest evidence that we have in its favor lies in the fact that Nietzki and Burckhardt[2] have prepared *colored* ethers (non-ionizable) of tetrabromphenolphthaleïn,

$$(C_2H_5O_2C.C_6H_4)(HOC_6H_2Br_2)C=C_6H_2Br_2=O,$$

and

$$(C_2H_5O_2C.C_6H_4)(C_2H_5OC_6H_2Br_2)C=C_6H_2Br_2=O,$$

with quinoïd molecules and a *colorless* lactoïd ether isomeric with the latter,

$$OCO.C_6H_4C(C_6H_4.OC_2H_5)_2.$$

A similar explanation applies to most, if not all, other indicators. Writers of books on physical chemistry must take into account such facts as those cited above, and as those established by Hantzsch.[3]

Ostwald's theory, admirable in most of its other details, would be in harmony with such facts, and the known general laws governing color in organic compounds, if sensitiveness to a change, for instance, of constitution, *involving a chromophoric group* under the influence of hydrogen or hydroxyl ions were substituted for sensitiveness merely to a change from a molecular to an ionic condition.

JULIUS STIEGLITZ.

[1] *Chem. Ztg.*, p. 1956 (1892).
[2] *Ber. d. chem. Ges.*, **30**, 175 (1897).
[3] *Ibid.*, **32**, 575, 3085, 3109 (1899).

AMERICAN STANDARD SPECIFICATIONS FOR STEEL. By ALBERT LADD COLBY. Sold by the writer, South Bethlehem, Pa. Price, $1.10.

This small book, of 103 pages, contains the revised text of the standard specifications adopted in August, 1901, by the American Section of the International Association for Testing Materials, accompanied by a critical review giving the reasons which governed the committee of the above association in forming its decisions. Since Mr. Colby was himself a member of this committee, the accuracy of the review adds greatly to the value of the work.

The requirements specified are grouped under seven general headings; *viz*: (1) Process of Manufacture; (2) Chemical Properties; (3) Physical Properties; (4) Test Pieces and Methods of Testing; (5) Finish and Variation in Weight; (6) Branding; (7) Inspection. Regarding (1), while the process is specified, the committee omitted restrictions as to the details of the processes, excepting in the case of steel rails. Regarding (2), carbon is omitted where tensile strength is specified, no limit in copper is specified, manganese and silicon are specified in special cases, sulphur in almost all cases, and phosphorus invariably.

Specifications are given for (1) steel castings; (2) axles; (3) forgings; (4) tires; (5) structural steel for buildings; (6) open-hearth boiler plate and rivet steel; (7) rails; (8) splice bars. These serve for the majority of uses to which steel is applied, and modifications may easily be made to suit particular cases.

Regarding chemical analysis, the specifications designate, in the case of each kind of steel, the location from which turnings or drillings are to be taken, but omit all suggestions as to the methods of analysis to be employed.

The book has a business-like appearance, and its contents are the result of so much deliberation by men of the highest qualifications, as to be practically above criticism. The specifications embody the acme of the most recent and most approved practice; their publication and consequent general acceptance as the American standards will save both manufacturers and consumers much misunderstanding, and this little book has hence an important mission to fulfil. The writer is to be congratulated on the satisfactory presentation of the matter which he has made.

J. W. RICHARDS.

GRUNDZÜGE DER SIDEROLOGIE, ZWEITER THEIL: ZUSAMMENHANG ZWISCHEN THERMISCHER UND MECHANISCHER BEARBEITUNG, KONSTITUTION UND EIGENSCHAFTEN DER EISENLEGIRUNGEN, VON HANNS FREIHERR VON JÜPTNER, Docent an der K. K. Bergakademie in Leoben. Leipzig: Verlag von Arthur Felix. 1901.

The first volume of this book, which was issued about one and a half years ago, treated of the morphological constituents, and of the physico-chemical ideas as applied to the constitution of iron alloys and slags. With the same care and completeness which characterized the first volume, the author, in the present book, deals with the relations which exist between the heat treatment and work to which iron or steel may be subjected in the process of manufacture, and the physical properties of the finished product. Since the introduction of physico-chemical ideas to the study of iron and steel, especially the idea of considering all alloys as solutions, the growth of the literature on the subject has been extremely rapid. Every person interested in the subject of iron and steel, whether from the point of view of the practical metallurgist or from the purely theoretical side, owes a debt of gratitude to Baron Jüptner for his splendid effort in arranging and systematizing the literature upon this subject. Since the appearance of the first volume, the theoretical knowledge has been so enriched by the applications of the phase rule to the explanation of the equilibrium phenomena, that it has been necessary for the author to give the important work of LeChatelier, Roozeboom, and others, as an introductory chapter in this volume. The book is divided into three parts: I. The influence of heat treatment and work upon the constitution of iron alloys. II. The physical properties of iron alloys in their connection with the chemical composition, the morphological structure, and the thermal and mechanical treatment. III. Relations between constitution, work, and mechanical properties of iron alloys.

In the first part is given a very complete and detailed discussion of Roozeboom's and LeChatelier's application of the phase rule to the study of the constitution of steel. It is extremely interesting to see that such a very practical subject as the steel industry should be receiving so much attention from those interested only in a purely scientific way. There can be no doubt of the fact that the industry will profit by the attention. In this part are also dis-

cussed Roberts-Austen's determinations of the critical points in electrolytic iron; the study of the effect of various elements—carbon, manganese, silicon, etc.—upon the character of the equilibrium curves; the relation between the temperatures of hardening and tempering, and the critical points. The influence of work and heat treatment upon the size of the grain is illustrated by the work of Sauveur on steel rails; and the effect of work above and below the critical range is also discussed. The chapter on segregation contains many interesting facts upon the unequal distribution of the elements among which the author has properly included the occluded gases.

The second part is a compilation of facts in regard to the physical properties of pure iron; specific gravity, melting point, latent heat, thermoelectric behavior, conductivity for electricity and heat, magnetism; and the influence of carbon, manganese, nickel, silicon, etc., on these various properties.

The third part deals with the purely mechanical properties such as tenacity, ductility, elasticity, and hardness and the effect of carbon and other elements upon these properties. Much of the data in Parts II and III are taken from the record of experiments finished before the recent rapid development of microscopic analysis, and consequently there is little relation shown between the properties of particular steels and its microscopic appearance. Future research in these fields will probably demand that the internal structure or morphological constitution be studied in connection with the various physical properties.

Throughout the text, references are always given to the original articles, and at the end of the book under the heading of the three separate parts, is a classified list of authors and their various contributions to the subject.

The book will undoubtedly be read with enthusiasm by all who have anything to do with this very interesting subject. It is to be hoped that the English translation which is under way will be worthy of the original.

HENRY FAY.

A LABORATORY GUIDE IN ELEMENTARY BACTERIOLOGY. By WILLIAM DODGE FROST, M.S. Second Edition. 1902. 348 pp. Published by the author.

This book contains substantially the material furnished by the author to students in bacteriology during two semesters at the University of Wisconsin.

Part I. General Bacteriology (132 pages) includes the elementary technique and direction for the usual systematic study of the biological characteristics of bacteria. Seven types are introduced representing the Saprophilic, Chromogenic, Zymogenic, Saprogenic and Phosphorescent classes of micro-organisms.

Part II. Medical Bacteriology (214 pages) includes the more specialized phases of the subject, particularly as applied to students preparing for medicine.

Outlines are given for the study of one or more forms typical of each of 22 groups, including all of the commonly met with pathogenic organisms.

In both parts of the guide, the forms are taken up in families or groups. An effort is made to have the student recognize the similarity between closely related forms and also to impress him with certain minute but important differences. The sequence of the types is good.

The general plan of the outline for each form is as follows: The organism is introduced with an explanatory note concerning habitat and a list of references to all of the leading English textbooks and occasionally to original sources. Following is an elaborate blank form or chart, covering four pages, for the permanent record, on the part of the student, of the observed morphological, cultural and physiological characteristics of the organism. This outlined chart indicates to the student what is to be done and provides for systematic notes and sketches. Throughout other parts of the book the right-hand pages are left for notes.

The general plan of the guide is good. The material for the fundamental exercises has been carefully selected. The directions for the execution of experiments are explicit and up to date. They bear evidence of having been subjected to class test before publication.

The cuts of apparatus are, for the most part, poorly executed,

and there is also occasional evidence of careless correction of proof.

The appearance of a second edition within a year is the best indication that this elementary laboratory guide fills a need.

ROBERT E. LYONS.

Prize of One Thousand Dollars.

The Association for Maintaining the American Women's Table at the Zoological Station at Naples, and for Promoting Scientific Research by Women, hereby announces the offer of a second prize of one thousand dollars, to be awarded in April, 1905, for the best thesis written by a woman, on a scientific subject, embodying new observations and new conclusions based on an independent laboratory research in biological, chemical or physical science.

The conditions of the competition may be learned by application to MRS. ELLEN H. RICHARDS, Massachusetts Institute of Technology, Boston, Mass.